

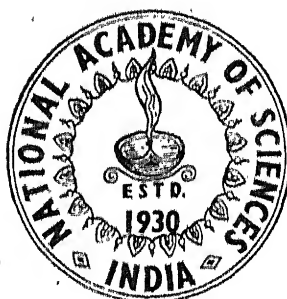
PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1957

VOL. XXVI

SECTION A

PART I

JANUARY 1957



NATIONAL ACADEMY OF SCIENCES, INDIA
ALLAHABAD

THE NATIONAL ACADEMY OF SCIENCES, INDIA

(Registered under Act XXI of 1860)

Founded 1930

Council for 1957

President

Prof. P. S. Gill, M.S., Ph.D., F.A.P.S., F.N.I., F.N.A.S.C., Aligarh.

Vice-Presidents

Prof. N. R. Dhar, D.Sc., F.R.I.C., F.N.I., F.N.A.S.C., Allahabad.

Prof. W. D. West, M.A., C.I.E., Sc.D., F.A.S., F.N.I., F.N.A.S.C., Saugor.

Honorary Treasurer

Prof. S. Ghosh, D.Sc., F.R.I.C., F.N.I., F.N.A.S.C., Allahabad.

Foreign Secretary

Dr. R. K. Saksena, D.Sc., F.N.I., F.N.A.S.C., Allahabad.

General Secretaries

Dr. R. N. Tandon, M.Sc., Ph.D., D.I.C., F.N.A.S.C., Allahabad.

Shri S. Basu, M.Sc., F.N.I., F.N.A.S.C., New Delhi.

Members

Prof. P. L. Srivastava, M.A., D.Phil., F.N.I., F.N.A.S.C., Allahabad.

Mrs. Savitri Sahni, M.Sc., F.N.A.S.C., Lucknow.

Prof. S. Ranjan, M.Sc., D.Sc., F.N.I., F.N.A.S.C., Allahabad.

Prof. A. K. Bhattacharya, D.Sc., F.R.I.C., F.N.A.S.C., Saugor.

Prof. K. Banerji, D.Sc., F.N.I., F.N.A.S.C., Allahabad.

Prof. R. Misra, M.Sc., Ph.D., F.N.I., F.N.A.S.C., Banaras.

Prof. M. D. L. Srivastava, D.Sc., F.N.A.S.C., Allahabad.

Shri M. S. Randhawa, M.Sc., F.N.I., F.N.A.S.C., I.C.S., New Delhi.

Prof. H. R. Mehra, M.Sc., Ph.D., F.N.I., F.N.A.S.C., Allahabad.

The Proceedings of the National Academy of Sciences, India, is published in two sections: Section—A (Physical Sciences) and Section—B (Biological Sciences). Six parts of each section are published annually.

The Editorial Board in its work of examining papers received for publication is assisted, in an honorary capacity, by a large number of distinguished scientists. Papers are accepted from members of the Academy *in good standing*. In case of a joint paper, one of the authors must be a member of the Academy. The Academy assumes no responsibility for the statements and opinions advanced by the authors. The papers must conform strictly to the rules for publication of papers in the *Proceedings*. A total of 50 reprints are supplied free of cost to the author or authors. The authors may have any reasonable number of additional reprints at cost price, provided they give prior intimation while returning the proof.

Communications regarding contributions for publication in the *Proceedings*, books for review, subscriptions, etc., should be sent to the General Secretary, The National Academy of Sciences, India, Lajpatrai Road, Allahabad-2 (India).

Annual Subscription for each Section: Rs. 30 (Inland); 60 sh. (Foreign)
Single Copy: Rs. 5 (Inland); 10 sh. (Foreign).

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA

1957

PART I]

SECTION A

[VOL. XXVI

ON THE MAXIMUM ATTAINABLE STELLAR
LUMINOSITIES

BY HARLOW SHAPLEY

(*Harvard Observatory, Cambridge, Massachusetts*)

Received on January 2, 1956

SOMETIMES we wish that all stars had the same candle power, preferably the luminosity of the sun, for then it would be simple to determine their distances from measures of their apparent brightness. The faintest stars would be the most remote and faintness would be a measure of distance. We could readily fathom our Milky Way. But such simplification would be attained only if there were no obscuring dust between the stars, no diminishing of light except the attenuation resulting from increasing distance. Under such ideal conditions the distance of a star (of the sun's candle power) would be simply $d = 10^{0.2m-0.1}$ in parsecs, or $d = 10^{0.2m+0.4}$ in light years, where m is its photographic apparent magnitude.

The stars, however, are not all of the same candle power, and there also is much trouble with light scattering caused by the dust in space. We are forced from a simple measuring of distance to a laborious examination of a great spread in candle power among stars. There are white dwarfs and lilliputian red stars that radiate at less than a ten-thousandth the rate of the sun, super-luminous stars a million times more radiant than the sun, and all the grades between. We can know little about the lilliputian stars, except

those in the immediate solar neighbourhood. The supergiants, however, can be examined throughout our whole Milky Way system and in the distant external galaxies, since their excessive brightness makes them accessible even though distant. We shall in this brief consideration speak only of those high luminosity objects that exceed the sun in candle power by more than a thousand times.

Supernovæ.—The greatest luminosity attained by a single star is the temporary brightness of a supernova at its maximum. Several of these explosive stars discovered in recent years have briefly equalled in radiation the total light of the galaxy in which they appear. Such objects, shining for a few hours or days with the radiation of more than that of a hundred million ordinary suns, provide extraordinary exhibitions of energy release—the most energetic displays in all the universe except possibly creation itself. The distances and total luminosities of the galaxies, which an occasional supernova can match in brightness, are difficult to estimate with accuracy, but an absolute magnitude of -14.5 is suggested as average. The absolute magnitude of the sun (photographic) is $+5.5$. The difference corresponds to 100,000,000 times in light emission.

In our own galaxy we commonly point to the Crab Nebula as the gaseous spreading nebula produced by the explosion of the supernova of 1054 A.D. And we believe that Tycho's nova of 1572 and Kepler's of 1604 were both of the supernova class. In some galaxies of the Sc class, two or three supernovæ have been recorded in a single generation, and in such systems "super-novation" must be in the long run of the millennia a very significant phase of stellar evolution.

Ordinary Novæ.—Supernovæ, as we see, are relatively rare phenomena. But the ordinary nova is not uncommon. If we watched the whole sky carefully, and took note of all large light variations brighter than the twelfth magnitude, we should be able to record at least thirty novæ a year in our galaxy, a large proportion of them in the Sagittarius star clouds of the southern Milky Way, that is, in the direction of the centre of our system. It is difficult as yet to estimate the distances and absolute magnitudes of these galactic novæ, except for those that have visible expanding shells. For them an average absolute magnitude of -7.6 has been derived. For the ordinary nova in the Andromeda Nebula the mean value is -7.5 . The almost exact agreement is probably accidental, since the numbers entering these means are small.

The novæ of the Magellanic Clouds give us the most reliable measure of the maximum luminosity attained by these afflicted stars when they blow

off their outer shells. The Harvard observers, who have had available several thousand photographs of the Star Clouds of Magellan made with half a dozen different instruments, have recorded only nine of these ordinary novæ (and no supernovæ) in the past half century. They appear to be surprisingly infrequent in these two irregular galaxies compared with the frequency in our own galactic system and in the Andromeda Nebula, both of which are Sb spiral galaxies.

The novæ in the Magellanic Clouds in the mean have the following absolute magnitudes:—

Small Cloud (4 novæ)	-7.8 ± 0.13 (m.e.)
Large Cloud (5 novæ)	-7.5 ± 0.11 (m.e.)

The fast rising novæ average to be somewhat brighter at maximum than those that rise more slowly from obscurity; but the evidence must be strengthened before we can say more than that the ordinary novæ appear to rise to about the same total brightness wherever they are found. That brightness in blue light is more than 150,000 times the candle power of the sun.

Eclipsing Stars.—The two Magellanic Clouds, of which we can, with modest telescopic power, get an objective point of view and see all the giant and supergiant stars, is the best place to search for the maximum luminosity attainable by all types of stars, and in particular by those close double stars that reveal their duplicity through eclipses. Mrs. Virginia Nail and I have made a study of fifty eclipsing variable stars in the two Clouds. We were able to confirm for most of these stars their physical membership in the Magellanic Clouds (rather than in our own galaxy) by means of a statistical study of the frequency of occurrence of eclipsing variables in star fields bordering the Clouds. For example, near the famous Tarantula Nebulosity, 30 Doradus, in the Large Cloud, we found a group of giant eclipsing stars with periods and light curves much alike and with absolute magnitudes of -3.8 .

In both Clouds the giant eclipsing stars were predominately of the β Lyræ type, with the curved maxima in their light curves indicating the ellipsoidal forms of the component stars. The ten brightest β Lyræ variables (4 in the Small, 6 in the Large) range in absolute magnitude from -4.15 to -6.45 , with a mean of -4.8 ± 0.23 (m.e.). We can be fairly sure from our surveys that no eclipsing binary exceeds -6.5 in absolute magnitude, or roughly 60,000 times the brightness of the sun. That value refers of course to the total light of both components; in most systems the total appears to be fairly evenly divided between the two.

Supergiant Red Variables.—The most voluminous stars in the neighbourhood of the sun are the class M reddish giants like Antares and Betelgeuse. Their radii exceed that of the earth's orbit. Also in candle power they are supergiantic. They are, however, exceeded in volume and luminosity by red stars in the Clouds of Magellan. Doubtless we would also find giants in our own galactic system that surpass them, if we could identify the distant supergiants among the millions of faint Milky Way stars and had a reliable method of measuring their distances and candle powers. Knowing the distance of the Magellanic Clouds, however, we can readily find the intrinsic luminosities of their brightest red variables, and discover also that many are more than 100,000,000 times the volume of the sun.

Among the red giant stars in the Magellanic Clouds are Cepheid variables of long period, Mira-type long period variables (but of small amplitude), irregular variables much like Betelgeuse, and many for which no appreciable variation has yet been recorded. The six brightest variables in the Small Cloud are Cepheids with Harvard Variable (HV) numbers, period lengths, and maximum absolute magnitudes as follows:—

HV 1956	209	days	—7.2	Mag.
„	821	127	„	—6.7 „
„	824	65.8	„	—6.7 „
„	834	73.5	„	—6.7 „
„	2195	41.8	„	—6.4 „
„	829	88.5	„	—6.3 „

The corresponding luminosities in terms of that of the sun range from 120,000 to 50,000, with a mean value of about 75,000.

The five brightest irregular variables of the Small Cloud have an absolute magnitude of —6.1 in the mean, and the five brightest of the Mira Class have the mean absolute magnitude of —4.5.

Equally high luminosities for red stars are found in the Large Cloud. In that system is one variable, S Doradus, which, for the time being, holds the record as the brightest known star. It has a peculiar spectrum and may be an eclipsing star with a very long period, but further photometric and spectroscopic study will be necessary before its peculiarities can be accurately diagnosed. The apparent photographic magnitude of S Doradus is approximately 9.0, absolute magnitude —10.0, and the corresponding candle power is more than a million times that of our sun. At its present rate of radiation its future life will be short compared with the predicted solar life. It is losing

mass through radiation at the rate of 5×10^{12} tons a second, or 15×10^{19} tons a year. In a mere million years S Doradus may be burned out and quite beyond the reach of terrestrial telescopes.

SUMMARY

The highest luminosities attained by stars are best evaluated through photometric studies of the Clouds of Magellan and of other nearby external galaxies. In terms of the sun's radiation as unity we find the following approximate values of the brightest supergiants:—

Cepheid variables	..	100,000
Eclipsing binaries	..	60,000
Irregular variables (red)	..	45,000
Long period variables	..	10,000

The foregoing values are in terms of ordinary photographic (blue) light. In red light the eclipsing binaries would be fainter, and the others much brighter than given above.

The brightest blue non-variable stars of the Magellanic Clouds, which are chiefly in the large star clusterings that we call Constellations and which have spectra of Class OB, rarely exceed the giant long period variables in light power.

The unstable stars, exploding novæ, rise to superlative luminosities. For their brief life-times as giants, the ordinary novæ attain a brightness equal to about 150,000 suns. The rare supernova for an interval of a few days or weeks often attains a brightness equal to a hundred million suns.

RECLAMATION OF ALKALI SOILS BY MIXTURES OF PHOSPHATES AND SUNN-HEMP

BY S. P. MITRA AND RAGHUBIR SINGH

(Sheila Dhar Institute of Soil Science, University of Allahabad)

Received on November 1, 1956

ALKALI soils are widely distributed in arid and semi-arid regions of the world and are commonly divided into (1) saline soil, (2) saline alkaline soil and (3) alkaline soil. The Regional Salinity Laboratory, Riverside, California,¹ designate these soils on the basis of the following specifications:

	pH	Conductivity in millimohs per c.m. at 25° C.	Ex-Na (Per cent. of total exchangeable cations)
Saline soil	.. <8.5	>4	≤15
Saline alkaline soil	.. 8.5	>4	≤15
Alkaline soil	.. >8.5	<4	≤15

Salinization of alkali soil refers to the accumulation of salts in the soil which is the first step in the formation of alkali soil. These salts are not detrimental to the structure, texture and permeability of the soil. In the second phase of the development of the alkali soil, salinization is accompanied by alkalization; and the texture and structure undergo deterioration, but, the usual permeability of the soil is maintained. Sodium carbonate begins to be produced in the third and the final stage of the development of the alkali soil. The texture and structure as well as permeability are completely destroyed with the evolution of alkali soil.

Alkali soils can be reclaimed by the removal of the causes of infertility, viz., high content of soluble salts, and by conversion of Na-clay into Ca-clay. The saline soils can be reclaimed by heavy leaching of the soil with water. Reclaiming of the saline soils by leaching is only possible in those localities where facility of good drainage is easily available. Alkaline soils can be reclaimed by the addition of large quantity of soil ameliorant accompanied by leaching. The most commonly used materials are gypsum, sulphur,

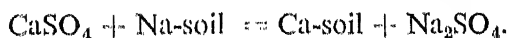
ferrous and aluminium sulphates, sulphuric acid and liquid sulphur dioxide. These substances change the Na-soil into calcium one.



The salts present and those formed during the process of reclamation are removed by leaching. So, the most important and essential part of the reclamation of alkaline and saline soil is the supply of good quality irrigation water and efficient system of drainage.

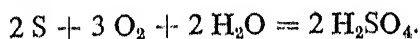
Some of the previous workers claimed that flooding of the soil with water and removal of the salts in drainage water can be employed in the reclamation of alkaline soil. In saline alkaline soil, leaching can bring about some improvement so long as there is sufficient amount of salts in the soil. When most of the salts are removed by leaching, permeability decreases and leaching becomes very slow and consequently no significant improvement is perceptible.

The most up-to-date method of alkali soil reclamation is the addition of soil ameliorant accompanied by leaching. Gypsum reacts with the sodium complex of alkali soil and converts it into Ca-soil. It also reacts with Na_2CO_3 present in the alkali soil and converts it into less injurious Na_2SO_4 .

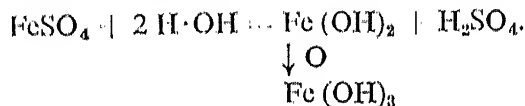


The beneficial effect of gypsum can only be obtained when Na_2SO_4 formed is removed by leaching, for, the solubility of gypsum in Na_2SO_4 solution is considerably lower than in water alone.

Sulphur incorporated in alkali soil is oxidised by sulphur bacteria into H_2SO_4 which partly neutralises the Na_2CO_3 present *in situ* and partly reacts with CaCO_3 to form CaSO_4 and CO_2 . This CaSO_4 reacts in the manner described above.



Ferrous and aluminium sulphates hydrolyse in water to form sulphuric acid which reacts with alkali soil as in the case of sulphur.



Liquid sulphur dioxide may be dissolved in irrigation water where it forms sulphurous acid and is then oxidised to sulphuric acid,

The soil ameliorants described above cannot be used by an average Indian farmer due to their high cost and unavailability. The alkali soil is usually deficient in carbon and nitrogen and, hence, for successful reclamation, the fertility level of this soil should also be increased. We have shown that by the addition of different soil amendments in conjunction with different organic matter alkali soil can be reclaimed fully. Organic matter increases the humus status of soil which increases the permeability and prevents the reversion into alkali soil.

The role of different phosphatic amendments incorporated with different organic materials has been studied by us in the reclamation of alkali soil.^{2,3}

EXPERIMENTAL

The alkali soil used in these experiments was collected from Soraon (a place approximately 13 miles from Allahabad). It was dried and sieved through 100 mesh. Sunn-hemp of 3-months-old sample with nodules were dried and chopped, first with a hand instrument and, finally, cut to small pieces with a mechanical chopper.

200 grams of alkali soil were taken in enamelled dishes and were mixed with 13 gm. of sunn-hemp. To each of the plates individual treatment of tricalcium phosphate [$\text{Ca}_3(\text{PO}_4)_2$], dicalcium phosphate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and Trichinopoly rock phosphate were added in 1% and 2% doses.

The estimation of exchangeable calcium was done by Hissink's method.⁴ pH was determined by a Beckman pH meter in a suspension of soil and water in the ratio of 1 : 2.5 after being shaken for one hour in a bottle. The estima-

TABLE I

Percentage chemical composition of soil used

Moisture	1.3900
Loss on ignition	2.5000
HCl insoluble	84.5100
Sesquioxide	7.0500
Fe_2O_3	3.3800
CaO	1.0600
MgO	1.3100
K_2O	1.1000
Available phosphate (2% citric acid)	0.0318
Total carbon	0.1350
Total nitrogen	0.0353
Exchangeable calcium	3.5720 m.e.
pH	10.00

tion of carbon was done by Robinson, McLeans and Williams method.⁵ Nitrogen was determined by Kjeldahl method.⁶ The available phosphate was determined in 2% citric acid extract⁷ of soil by Lorenz method.⁸

TABLE II

Analysis of water extract of the soil (per cent.)

Total soluble salts	..	0.8960
Carbonate	0.1347
Bicarbonate	0.4376
Chloride	0.0302
Sulphate	0.0060

TABLE III

Analysis of Sunn-hemp and Rock phosphate in per cent.

	Sunn-hemp	Rock phosphate
Carbon	.. 37.701	..
Nitrogen	.. 1.232	..
CaO	.. 2.100	20.810
MgO	.. 0.160	1.760
P ₂ O ₅	.. 1.518	27.470

TABLE IV

200 gm. Soil + 13 gm. Sunn-hemp

Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Ex-Ca in m.e. %	Available P ₂ O ₅ %	pH
0	2.4700	0.0902	..	3.241	0.0295	10.00
60	1.9264	0.0613	22.00	4.203	0.0354	9.80
120	1.8202	0.0594	26.31	4.815	0.0395	9.70
210	1.7001	0.0573	32.00	5.224	0.0427	9.40
300	1.5032	0.0542	43.00	5.835	0.0458	9.10
390	1.3054	0.0523	47.11	5.843	0.0487	9.00

TABLE V

200 gm. Soil + 13 gm. Sunn-hemp + 1.0% Tricalcium phosphate

Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Ex-Ca in m.e. %	Available P_2O_5 %	pH
0	2.4700	0.0902	..	3.241	0.0317	10.00
60	1.8275	0.0785	26.01	5.812	0.0347	9.40
120	1.5851	0.0758	35.83	6.401	0.0425	8.80
210	1.4287	0.0728	42.16	6.825	0.0452	8.40
300	1.2857	0.0728	48.00	7.234	0.0478	8.20
390	1.1434	0.0714	53.71	7.654	0.0514	8.00

TABLE VI

200 gm. Soil + 13 gm. Sunn-hemp + 2.0 %Tricalcium phosphate

Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Ex-Ca in m.e. %	Available P_2O_5 %	pH
0	2.4700	0.0902	..	3.241	0.0391	10.00
60	1.7561	0.0795	28.90	6.223	0.0454	9.30
120	1.5494	0.0795	37.27	6.823	0.0454	8.70
210	1.3354	0.0768	46.00	7.154	0.0486	8.30
300	1.1143	0.0768	54.88	7.456	0.0514	8.10
390	1.0378	0.0768	59.94	7.935	0.0536	7.90

TABLE VII

200 gm. Soil + 13 gm. Sunn-hemp + 1.0% Dicalcium phosphate

Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Ex-Ca in m.e. %	Available P_2O_5 %	pH
0	2.4700	0.0902	..	3.241	0.0340	10.00
60	1.9457	0.0792	21.23	6.543	0.0423	8.80
120	1.7134	0.0758	30.63	7.235	0.0423	8.70
210	1.5045	0.0735	39.10	7.904	0.0454	8.05
300	1.2843	0.0718	48.00	8.405	0.0486	7.90
390	1.1164	0.0718	54.80	8.807	0.0504	7.70

TABLE VIII

200 gm. Soil + 13 gm. Sunn-hemp + 2.0% Dicalcium phosphate

Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Ex-Ca in m.e. %	Available P_2O_5 %	pH
0	2.4700	0.0902	..	3.241	0.0378	10.00
60	1.9365	0.0823	21.60	6.904	0.0455	8.70
120	1.7054	0.0775	30.95	7.543	0.0455	8.30
210	1.5458	0.0775	37.42	8.025	0.0484	8.00
300	1.2805	0.0754	48.16	8.405	0.0513	7.80
390	1.1124	0.0754	55.00	8.815	0.0536	7.60

TABLE IX

200 gm. Soil + 13 gm. Sunn-hemp + 1.0% Trichinopoly Rock phosphate

Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Ex-Ca in m.e. %	Available P_2O_5 %	pH
0	2.4700	0.0902	..	3.241	0.0332	10.00
60	1.7575	0.0785	28.85	5.643	0.0425	9.50
120	1.5330	0.0763	38.00	6.401	..	8.85
210	1.4054	0.0735	43.10	6.932	0.0455	8.50
300	1.2545	0.0705	49.20	7.125	..	8.40
390	1.1334	0.0705	54.11	7.325	0.0513	8.20

TABLE X

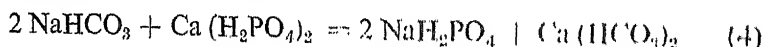
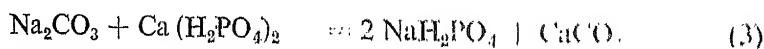
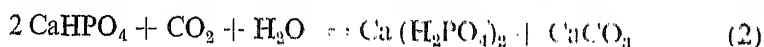
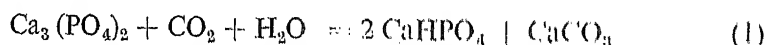
200 gm. Soil + 13 gm. Sunn-hemp + 2.0% Trichinopoly Rock phosphate

Period of exposure in days	Total carbon %	Total nitrogen %	Carbon oxidised %	Ex-Ca in m.e. %	Available P_2O_5 %	pH
0	2.4700	0.0902	..	3.241	0.0354	10.00
60	1.7075	0.0810	30.87	5.643	0.0425	9.30
120	1.4946	0.0798	39.50	6.453	..	8.70
210	1.3254	0.0781	46.34	7.023	0.0446	8.40
300	1.2006	0.0754	51.40	7.523	..	8.10
390	1.0135	0.0732	59.00	7.828	0.0525	7.90

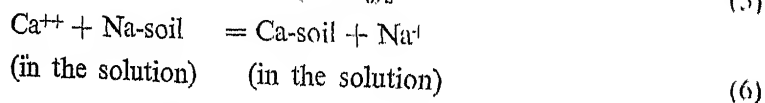
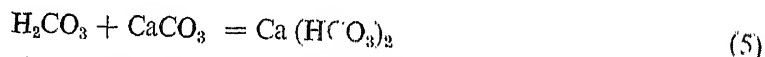
DISCUSSION

A perusal of the foregoing results shows that addition of sunn-hemp (*Crotalaria juncea*) in combination with rock phosphate and different phosphatic compounds brings about a remarkable change in the pH, exchangeable calcium, available phosphate, and carbon and nitrogen status of alkali soil.

The pH of the soil shows a radical change after the application and during the decomposition of different phosphatic compounds in conjunction with sunn-hemp as organic matter in the system. The pH after 390 days in case of dicalcium phosphate, tricalcium phosphate and rock phosphate is 7.60, 7.90 and 7.90 respectively. This phenomenon can be explained by the fact that CO_2 is generated during the decomposition of sunn-hemp which reacts with phosphates converting them into more soluble phosphatic compounds. These new phosphatic substances generated in the system react with Na_2CO_3 and NaHCO_3 of alkali soil converting them into NaH_2PO_4 and thereby neutralising the soil alkali. That is why the fall of pH is always noticed in these reclamation experiments.

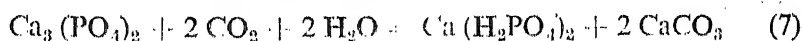


The CO_2 generated during the decomposition of sunn-hemp is converted into H_2CO_3 in presence of water. This weak acid reacts with CaCO_3 present in rock phosphate forming $\text{Ca}(\text{HCO}_3)_2$ and thereby more Ca^{++} is brought into solution. From equations (1) and (2) it is clear that tricalcium phosphate and dicalcium phosphate give Ca^{++} in the solution by the action of CO_2 and water. These soluble Ca^{++} replace Na^+ from the exchange complex of alkali soil converting it into calcium soil and, hence, increase in exchangeable calcium status of alkali soil is always observed during the course of these experiments. Kelley⁹ obtained similar results by growing Bermuda grass in alkali soil.



The increase in available phosphate may be due to the fact that during the process of oxidation of organic matter CO_2 produced reacts with trical-

cium phosphate forming dicalcium phosphate and monocalcium phosphate respectively. This is clear from the equations (1) and (7):—



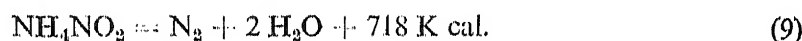
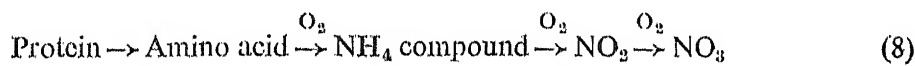
Dicalcium phosphate forms monocalcium phosphate only (equation 2). The order of solubilities of the three phosphates is as follows:—



The increase in available phosphate in these experiments is explained by the fact that less soluble phosphates are converted into more soluble ones by the action of CO_2 and water.

The oxidation of organic matter varies directly with the alkalinity of the different phosphatic compounds added in the system. Maximum oxidation was found in the samples treated with rock phosphate. Dicalcium phosphate treated sample had the least oxidation.

The loss of nitrogen may be explained from the view point that in the process of nitrification of proteins taking place in the experiments an intermediary unstable substance, ammonium nitrite, is formed which decomposes into nitrogen gas and water causing loss of nitrogen in the system.



The loss of nitrogen is brought about by the microbiological activities as well as photochemical agencies.¹⁰ Uptil now it was believed that loss of nitrogen is brought about only by bacterial metabolism.

Ingham¹¹ has reported the phenomena of nitrification and denitrification in the following words:—

“In the soils examined, nitrification is attributed largely to photochemical oxidation at the soil surface. Denitrification may result from the spontaneous decomposition of NH_4 and NO_2 ions during the drying out of soils in which the appropriate ions occur respectively.”

Dhar^{12, 13} has reported in a number of papers where he emphasized the process of nitrification and nitrogen loss as a photochemical process.

It is very interesting to note that loss of nitrogen in case of a soil treated with sunn-hemp is more than that of a soil treated with sunn-hemp *plus* phosphatic compounds. It is believed that in presence of large amount of phosphate in the system, a stable phospho-protein is formed which resists ammoni-

fication and nitrification. Thus, the loss of nitrogen is less when alkali soils are treated with mixtures of sunn-hemp and phosphates than when treated with sunn-hemp alone.

REFERENCES

1. RICHARDS, L. A., 1954, *Diagnosis and Improvement of Saline and Alkaline Soils* (United States Department of Agriculture).
2. MITRA, S. P., GHOSH, S. K. AND SINGH, R., 1955, *Proc. Nat. Acad. Sci.*, **24 A**, 647-50.
3. — AND SINGH, R., 1955, *Ibid.*, **24 A**, 677-89.
4. HISSINK, D. J., 1923, *Soil Sci.*, **15**, 269-76.
5. ROBINSON, G. W., MCLEANS, W. AND WILLIAMS, R., 1929, *Jour. Agric. Sci.*, **29**, 315.
6. TREADWELL, F. P., AND HALL, W. T., 1947, *Analytical Chemistry*, Part II, (John Wiley), 493-94.
7. DYER, B., 1894, *Trans. Chem. Soc.*, **65**, 115-67.
8. PIPER, C. S., 1947, *Soil and Plant Analysis*, 150-53.
9. KELLEY, W. P., 1951, *Alkali Soil* (Reinhold Publication Corporation, New York, U.S.A.).
10. CORBET, A. S., 1934, *Biochem. Jour.*, **28**, 1575.
11. INGHAM, G., 1938, *Jour. Sci. African Chem. Inst.*, **21**, 59-63.
12. DHAR, N. R. AND RAO, G. G., 1931, *Soil Sci.*, **31**, 379.
13. —, TANDON, S. P. AND MUKERJEE, S. K., 1935, *Jour. Ind. Chem. Soc.*, **12**, 67.

ON CHOICE OF INTERNAL STANDARD IN QUANTITATIVE SPECTRO-CHEMICAL ANALYSIS

J. K. ZOPE AND J. D. RANADE

(*Department of Physics, University of Saugar*)

Received on December 28, 1955

QUANTITATIVE spectro-chemical analysis is based on the fact that under given conditions, the intensity of a line of an element is directly proportional to the number of the emitting atoms, and hence to the quantity of the element present, provided all atoms are excited. An accurate quantitative analysis is done by utilizing the principle of internal standardization first introduced by W. Gerlach.¹ The advantage of an internal standard is that it compensates for various factors which affect the quantitative estimation.

The intensity of the spectral lines of an element has been known to be influenced by the presence of other elements which make up the sample. This effect is known as extraneous element effect. This effect has been studied by some workers²⁻⁴ in arc and spark spectra. There are certain elements which decrease the intensity of the lines of the test element, while others increase the intensity of the same lines. Some elements have no effect on the intensity of the lines of the test element even if present in sufficient quantity.

Here as an example, we have taken calcium and potassium as the extraneous elements and manganese as the test element. Iron is the internal standard. It is shown that the ratio of the intensity of manganese line to that of iron remains practically constant for all samples, containing varying quantity of extraneous element. If this ratio is taken as a measure of concentration of manganese in any sample it should be independent of the concentration of extraneous element in that sample; and thus this will be a guide to choose a proper internal standard in quantitative estimation.

EXPERIMENTAL

The samples are prepared by taking a constant quantity of manganese chloride (1.0 gm.) and varying the quantity of potassium and calcium carbonate from 0.01–0.5 gm. respectively. The internal standard iron oxide (0.01 gm.) was added to each sample in constant proportion. The graphite electrodes used for excitation of the samples were of small diameter as the spark runs very smoothly and reproducibility is improved. The spectrograms

were photographed on Ilford ordinary plates using Hilger Intermediate quartz spectrograph.

The iron line 2621.8 \AA , stepped in intensity with the help of a step filter, is used for the calibration curve. Dr. Lange's microphotometer has been used for the density measurements of the manganese lines (2576.1 \AA) and the iron line (2611.8 \AA) respectively. The standard procedure is followed for the determination of intensity of manganese and iron lines. The ratio of the intensity of the manganese line for a given concentration of the extraneous element, to the intensity of the same line when the sample contains no extraneous element is calculated. This ratio is called ' f '. The deviation of the magnitude of this ratio from unity is taken as a measure of the effect of the extraneous element. For each extraneous element curves are drawn between the ' f ' values and the concentration of the extraneous element.

If in the absence of the extraneous element the intensity of a line is I_1 and the intensity of the internal standard line is I_2 then the intensity ratio R is given by

$$R = \frac{I_1}{I_2}.$$

Now if an extraneous element is added the intensity of the test element is changed and becomes $I_1 f_1$ and that of the internal standard line becomes $I_2 f_2$ and the new Ratio is

$$R_1 = \frac{I_1 f_1}{I_2 f_2}.$$

Table I gives the values of ' f ' for manganese line and iron line respectively, when potassium is used as an extraneous element. Table II gives similar values for manganese and iron lines when calcium is an extraneous element.

TABLE I

Source.—Condensed spark; Extraneous element—Potassium; Internal standard—Iron; Test element—Manganese.

No.	% K_2CO_3	Fe 2611.8 f	Mn 2576.1 f_1	R_1 Calculated	R_2 Predicted
1	0	1.0	1.0	1.4	1.41
2	5	1.12	0.86	1.06	1.00
3	10	0.75	0.79	1.47	1.47
4	15	0.75	0.79	1.47	1.48
5	25	0.56	0.70	1.75	1.75
6	35	0.40	0.64	1.60	1.60

TABLE II

Source.—Condensed spark; Extraneous element—Calcium.

No.	% CaCO ₃	Fe 2611.8 <i>f</i>	Mn 2576.1 <i>f</i> ₁	R ₁ Calculated	R ₂ Predicted
1	0	1.0	1.0	1.38	1.38
2	5	0.32	0.40	1.80	1.81
3	10	0.21	0.35	2.35	2.38
4	20	0.18	0.27	2.0	2.10
5	25	0.17	0.24	2.10	2.11
6	35	0.14	0.20	1.98	2.00

SOURCE :— CONDENSED SPARK .

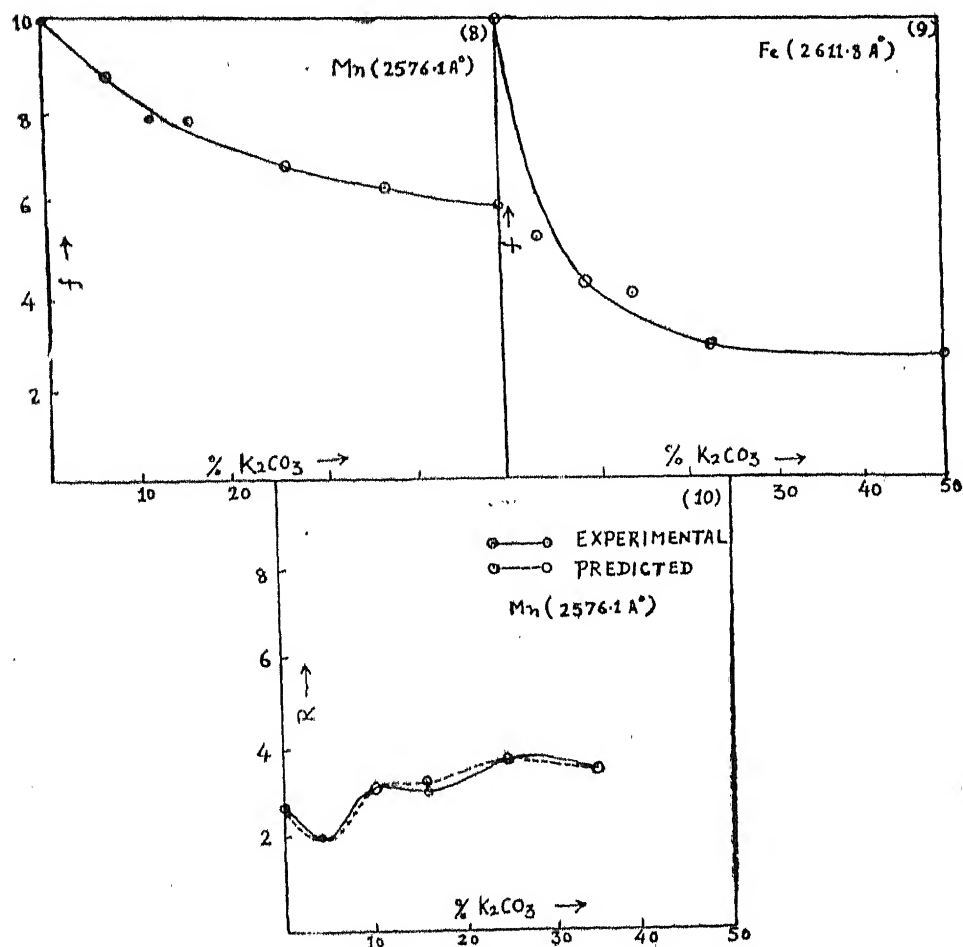


FIG. 1

DISCUSSION

Curves 8, 9 in Figure 1 and curves 14, 15 in Figure 2 show the variation in intensity of manganese and iron lines as the concentration of the extraneous Ca and K varies. From these it is clear that the intensity of the lines

SOURCE :- CONDENSED SPARK

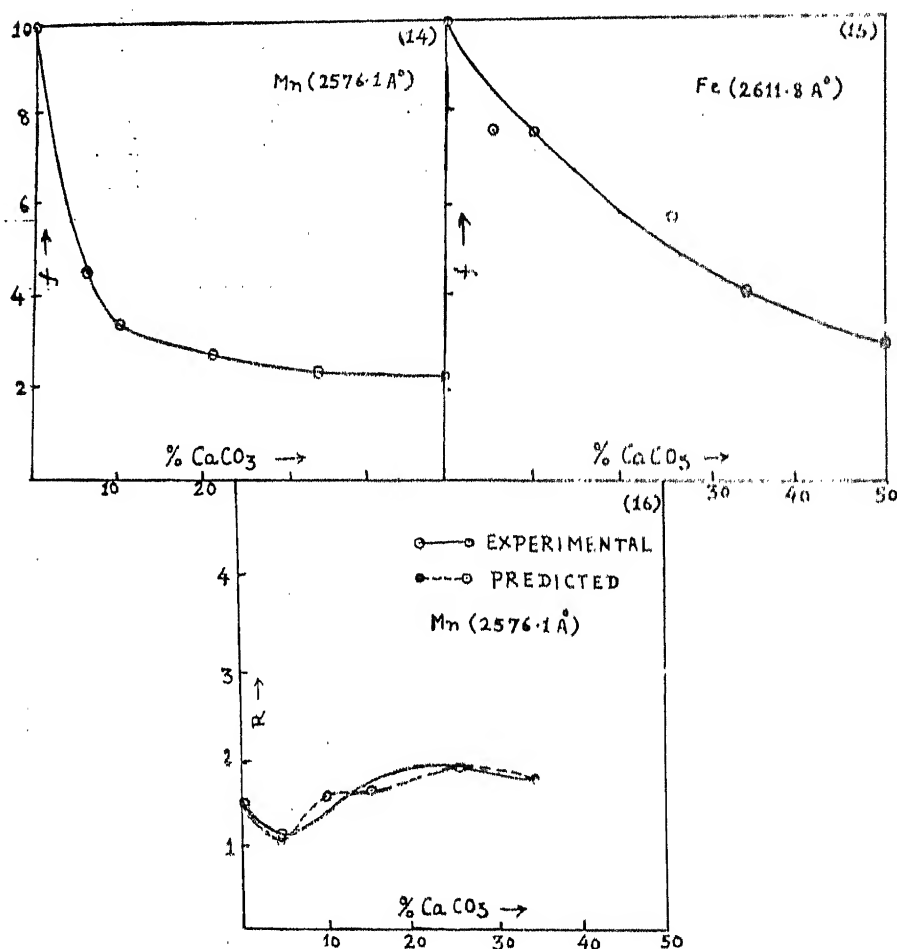


FIG. 2

of manganese and iron decreases with the concentration of the extraneous elements in the sample. This decrease is caused by the lowering of the effective temperature of spark by the presence of the elements Ca and K whose $i.p.s$ are less than that of manganese and iron. Now if we consider the ratio R , it is seen from curves 10, 16 that R remains practically constant for all the concentrations of the extraneous elements. It will be clear from this that it

is worthwhile to study the effect of extraneous elements by finding the R values. If R remains appreciably constant, the choice of internal standard is correct.

REFERENCES

1. GERLACH, W., 1929, *Foundation in Methods of Chemical Analysis by the Emission Spectrum* (Adam Hilger).
2. BRODE, W. R. AND HODGE, E. S., 1941, *Jour. Opt. Soc. Amer.*, **31**, 158.
3. LANGSTROTH, G. O. AND ANDRYCHUCK, D., 1948, *Cand. Jour. Rev.*, **26**, 39.
4. DUFFENDACK, O. S. AND WILEY, F. H., OWENS, J. S., 1935, *Indust. Eng. Chem. Anal.*, (Ed.), **7**, 40.

COMPOSITION AND STABILITY OF LEAD ALIZARIN SULPHONATE COMPLEX: A SPECTROPHOTOMETRIC STUDY

BY ANIL K. MUKHERJI AND ARUN K. DEY

(Chemical Laboratories, University of Allahabad, Allahabad)

Received on November 15, 1956

ABSTRACT

Alizarin Red S yields coloured complexes with many inorganic cations and has found application as a colorimetric reagent for the determination of aluminium, uranium and thorium. The colour reactions, however, are not specific and are subject to interference by various metallic ions. The present authors have reported the production of a purple coloured complex of the dye with lead ions and have observed that the coloured complex has a maximum absorption at 490 m μ .

In the present paper the formation of lead alizarin sulphate has been investigated by the spectrophotometric method using Unicam SP 500 Spectrophotometer. It has been observed that the Beer's law is not rigidly obeyed with different mixtures having varying amounts of lead and a large excess of the dye. Thus the dye cannot be recommended as a colorimetric reagent for the determination of lead.

The composition of the complex has been studied by the Job's method of continuous variation and it is found that the complex has the composition with the reactants in the ratio of 1:1. The value of formation constant at 28° C. has been calculated to be 5.0×10^4 , and the free energy of formation—6.4 Kcal.

The structure of lead alizarin sulphate has been discussed and it has been suggested that the two phenolic hydrogens are replaced by bivalent lead to form the complex.

SODIUM alizarin sulphate (Alizarin Red S) yields characteristic coloured complexes with various inorganic cations. This property has found application in the colorimetric determination of inorganic cations in dilute solutions.¹ Alizarin Red S has widely been employed for the colorimetric determination of aluminium,² and the interference of various ions on the colour has been discussed by Parker and Goddard.³ Raghava Rao *et al.* studied the complex formation between Alizarin Red S and uranium⁴ and thorium⁵ and recommended the dye as a suitable colorimetric reagent for the estimation of these metals. Ware⁶ in an important paper tested the application

of various colorimetric reagents for the determination of uranium and concluded that Alizarin Red S should not be used for uranium determinations. In a recent publication Mukherji and Dey⁷ have shown that Alizarin Red S produces a purple colour with lead nitrate having a maximum absorption at 490 m μ . In the same paper the authors have investigated the effect of pH changes on the colour of the dye and have sought to explain the colour changes on the basis of Kuhn's formula⁸ and discussed the different ionizing structures in the presence of varying concentrations of hydrogen ions.

In this paper we are presenting our results on the spectrophotometric study of the system $\text{Pb}(\text{NO}_3)_2$ —sodium alizarin sulphonate using various concentrations of the reactants. The composition and structure of the complex formed have been discussed and the formation constant and the free energy of formation of the complex have been calculated at 28° C.

EXPERIMENTAL

Standard solutions of lead nitrate B.D.H. AnalaR and Alizarin Red S B.D.H. indicator were prepared using double distilled water. For the measurement of optical density Unicam SP 500 Spectrophotometer was employed and the measurements conducted in an air-conditioned room maintaining a constant temperature of 28° C. The individual solutions were kept immersed in a thermostat maintaining a temperature of $28^\circ \pm 0.1^\circ \text{C}$ and the mixtures were kept at least for 15 minutes after mixing to attain equilibrium. For every measurement 1 cm. thickness of the solutions were used in glass cells supplied along with the instrument.

Validity of Beer's law.—In a set of experiments to a fixed quantity of the dye were added varying quantities of $\text{Pb}(\text{NO}_3)_2$ solution keeping in view that the amount of the dye always remained in large excess as compared to that of $\text{Pb}(\text{NO}_3)_2$. The total volume was made constant by the addition of water and the optical densities of different mixtures measured at a wavelength of 490 m μ . The observations were repeated at different concentrations of the dye and $\text{Pb}(\text{NO}_3)_2$ and it was concluded that Beer's law is not rigidly obeyed.

Nature of complexes formed.—In another set of experiments mixtures containing varying proportions of lead: Alizarin Red S (*i.e.*, 1:1, 1:2, 1:3, etc.) were prepared and the optical densities of the solutions at different wavelengths in each case measured. It was found that in all the cases the maximum absorption occurred at a spectral region of 490 m μ , which goes to prove that only one complex is formed with the reagent.⁹

Composition of the complex.—In order to determine the composition of the coloured complex Job's method of continuous variation¹⁰ was adopted. The

total volume in each case was kept 50 ml. The results are given in the following tables. The optical densities were measured at 490 m μ .

TABLE I

Concentration of Pb(NO₃)₂ (c) .. 5.0 \times 10⁻⁴ M
 Concentration of the dye (c') .. 5.0 \times 10⁻⁴ M
 pH of the mixtures 3.7-4.2
 $p = c'/c = 1$

Volume of Pb(NO ₃) ₂ in ml.	Volume of the dye in ml.	Optical density of the mixture (a)	Optical density of the dye (b)	Difference in optical density (a - b)	Remarks
0	50	0.190	0.190	..	The peak of the curve occurs at a ratio of 1:1 (Fig. 1, Curve A)
5	45	0.260	0.180	0.080	
10	40	0.270	0.160	0.110	
15	35	0.310	0.140	0.170	
20	30	0.350	0.125	0.225	
25	25	0.355	0.110	0.245	
30	20	0.330	0.100	0.230	
35	15	0.290	0.090	0.200	
40	10	0.220	0.070	0.150	
45	5	0.120	0.060	0.060	

TABLE II

Concentration of Pb(NO₃)₂ (c) .. 2.5 \times 10⁻⁴ M
 Concentration of the dye (c') .. 2.5 \times 10⁻⁴ M
 pH of the mixtures 4.0-4.8
 $p = c'/c = 1$

Volume of Pb(NO ₃) ₂ in ml.	Volume of the dye in ml.	Optical density of the mixture (a)	Optical density of the dye (b)	Difference in optical density (a - b)	Remarks
0	50	0.140	0.140	..	The peak of the curve occurs at a ratio of 1:1 (Fig. 1 Curve B)
5	45	0.150	0.135	0.015	
10	40	0.155	0.120	0.035	
15	35	0.160	0.105	0.055	
20	30	0.170	0.095	0.075	
25	25	0.180	0.070	0.110	
30	20	0.165	0.065	0.100	
35	15	0.135	0.060	0.075	
40	10	0.110	0.045	0.065	
45	5	0.060	0.025	0.035	

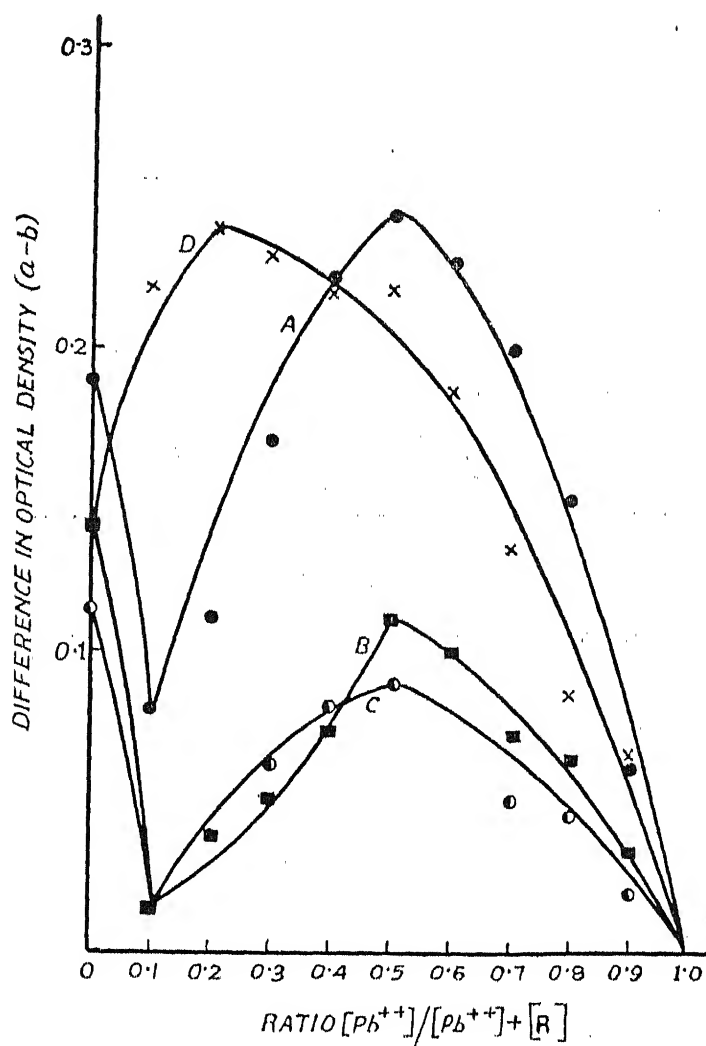


FIG. 1. Graphical determination of the composition of lead alizarin sulphonate complex. $\lambda = 490 \text{ m}\mu$. Curve A: $c = 5.0 \times 10^{-4} \text{ M}$, $p = 1$; Curve B: $c = 2.5 \times 10^{-4} \text{ M}$, $p = 1$; Curve C: $c = 2.0 \times 10^{-4} \text{ M}$, $p = 1$; Curve D: $c = 1.0 \times 10^{-4} \text{ M}$, $p = 2.5$.

TABLE III

Concentration of $\text{Pb}(\text{NO}_3)_2$ (c) .. 2.0×10^{-4} M
 Concentration of the dye (c') .. 2.0×10^{-4} M
 pH of the mixtures 4.4-5.0
 $p = c'/c = 1$

Volume of $\text{Pb}(\text{NO}_3)_2$ in ml.	Volume of the dye in ml.	Optical density of the mixture (a)	Optical density of the dye (b)	Difference in optical density (a - b)	Remarks
0	50	0.115	0.115	..	The peak of the curve occurs at a ratio of 1:1 (Fig. 1, Curve C')
5	45	0.120	0.105	0.015	
10	40	0.130	0.095	0.035	
15	35	0.145	0.085	0.060	
20	30	0.150	0.070	0.080	
25	25	0.165	0.066	0.090	
30	20	0.140	0.055	0.095	
35	15	0.095	0.045	0.050	
40	10	0.075	0.030	0.045	
45	5	0.045	0.025	0.020	

TABLE IV

Concentration of $\text{Pb}(\text{NO}_3)_2$ (c) .. 4.0×10^{-4} M
 Concentration of the dye (c') .. 2.0×10^{-4} M
 pH of the mixtures 4.4-4.9
 $p = c'/c = 0.5$

Volume of $\text{Pb}(\text{NO}_3)_2$ in ml.	Volume of the dye in ml.	Optical density of the mixture (a)	Optical density of the dye (b)	Difference in optical density (a - b)	Remarks
0	50	0.120	0.120	..	The peak of the curve occurs at a ratio of 1:1 (Fig. 2, Curve B)
5	45	0.130	0.105	0.025	
10	40	0.145	0.095	0.050	
15	35	0.170	0.085	0.085	
20	30	0.185	0.070	0.115	
25	25	0.175	0.065	0.110	
30	20	0.165	0.055	0.110	
35	15	0.130	0.045	0.085	
40	10	0.100	0.030	0.070	
45	5	0.055	0.025	0.030	

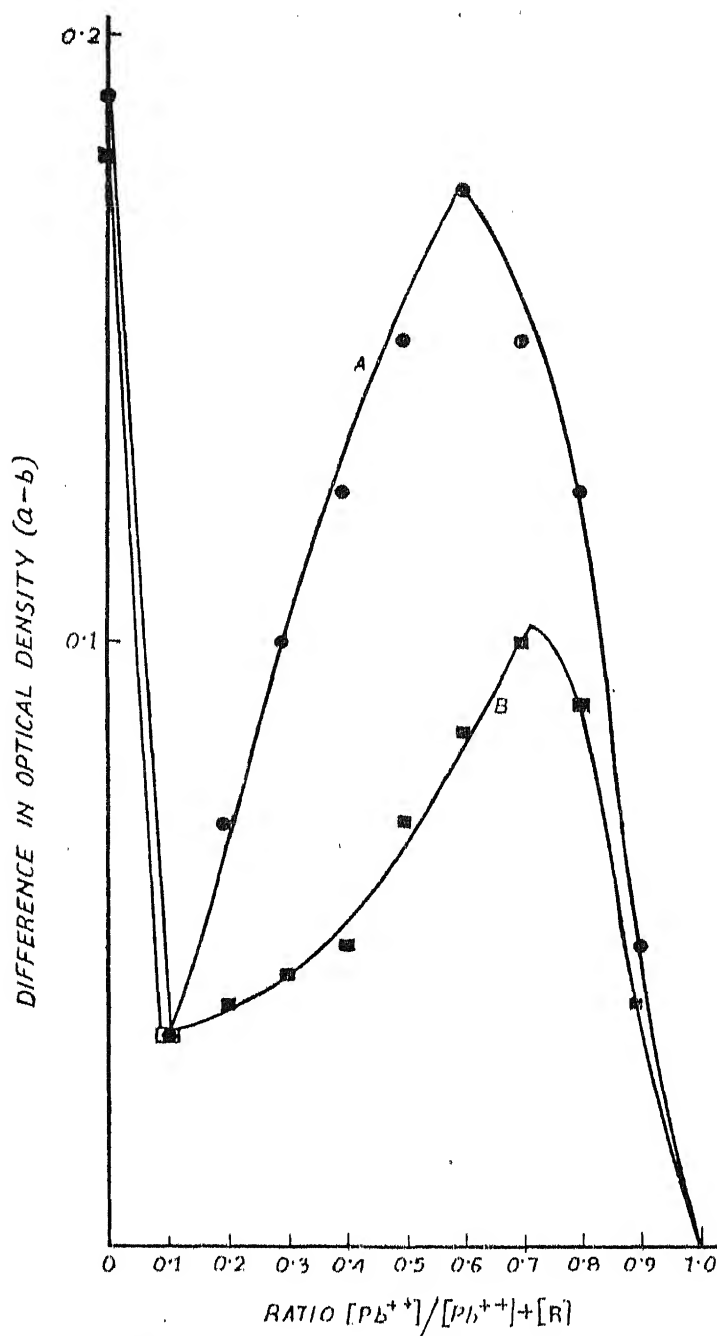


FIG. 2. Graphical determination of the composition lead alizarin sulphonate complex, $\lambda = 490 \text{ m}\mu$. Curve A: $c = 5.0 \times 10^{-4} \text{ M}$, $p = 0.66$; Curve B: $c = 4.0 \times 10^{-4} \text{ M}$, $p = 0.5$.

TABLE V

Concentration of $\text{Pb}(\text{NO}_3)_2$ (c) .. $5.0 \times 10^{-4} \text{ M}$
 Concentration of the dye (c') .. $3.33 \times 10^{-4} \text{ M}$
 pH of the mixtures 3.9-4.2
 $p = c'/c = 0.66$

Volume of $\text{Pb}(\text{NO}_3)_2$ in ml.	Volume of the dye in ml.	Optical density of the mixture (a)	Optical density of the dye (b)	Difference in optical density (a - b)	Remarks
0	50	0.190	0.190	..	The peak of the curve occurs at a ratio of 1:1 (Fig. 2, Curve A)
5	45	0.200	0.175	0.025	
10	40	0.220	0.160	0.060	
15	35	0.250	0.140	0.110	
20	30	0.280	0.115	0.165	
25	25	0.260	0.105	0.155	
30	20	0.235	0.085	0.150	
35	15	0.210	0.070	0.140	
40	10	0.160	0.050	0.110	
45	5	0.085	0.035	0.050	

TABLE VI

Concentration of $\text{Pb}(\text{NO}_3)_2$ (c) .. $3.33 \times 10^{-4} \text{ M}$
 Concentration of the dye (c') .. $5.00 \times 10^{-4} \text{ M}$
 pH of the mixtures 3.7-4.2
 $p = c'/c = 1.5$

Volume of $\text{Pb}(\text{NO}_3)_2$ in ml.	Volume of the dye in ml.	Optical density of the mixture (a)	Optical density of the dye (b)	Difference in optical density (a - b)	Remarks
0	50	0.190	0.190	..	The peak of the curve occurs at a ratio of 1:1 (Fig. 3, Curve A)
5	45	0.215	0.180	0.035	
10	40	0.230	0.160	0.070	
15	35	0.240	0.140	0.100	
20	30	0.250	0.125	0.125	
25	25	0.260	0.110	0.150	
30	20	0.275	0.100	0.175	
35	15	0.240	0.090	0.150	
40	10	0.195	0.070	0.125	
45	5	0.110	0.060	0.050	

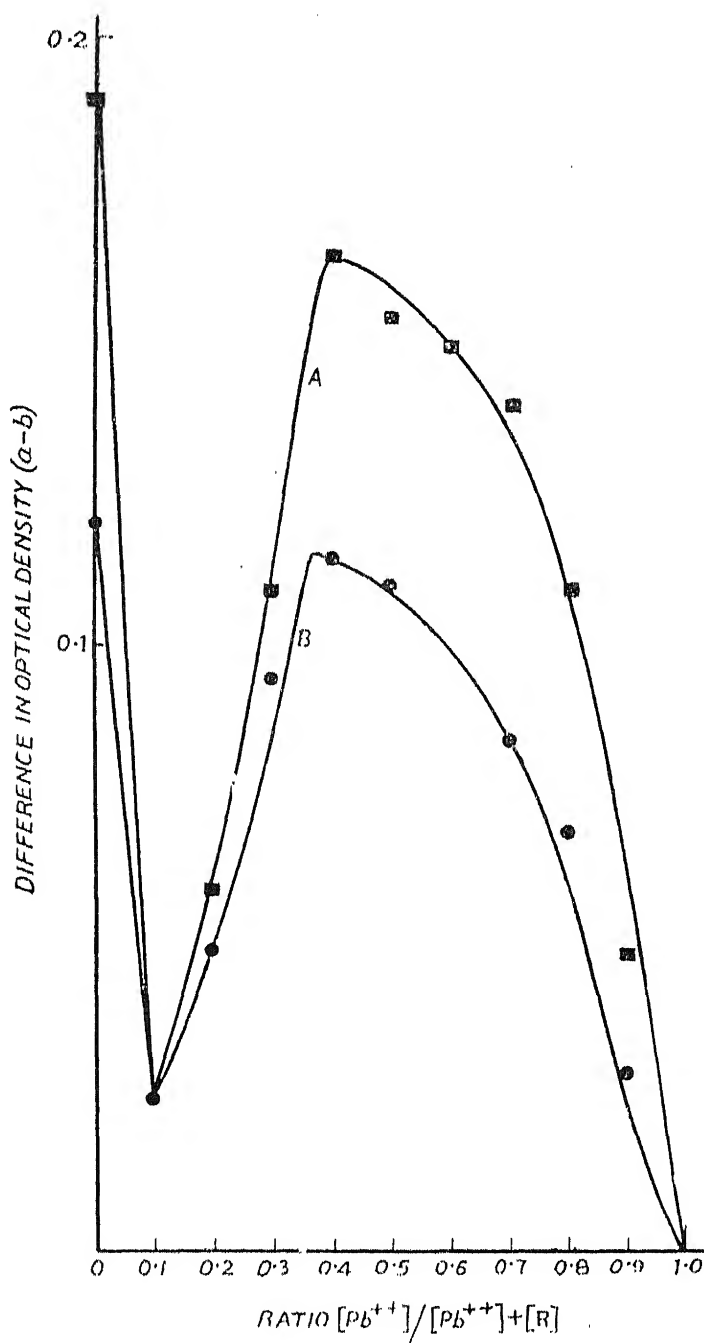


FIG. 3. Graphical determination of the composition of lead alizarin sulphonate complex, $\lambda_{\text{max}} = 490 \text{ m}\mu$, Curve A: $c = 3.33 \times 10^{-4} \text{ M}$, $p = 1.5$; Curve B: $c = 2.0 \times 10^{-4} \text{ M}$, $p = 2$.

TABLE VII

Concentration of $\text{Pb}(\text{NO}_3)_2$ (c) .. 2.0×10^{-4} M
 Concentration of the dye (c') .. 4.0×10^{-4} M
 pH of the mixtures 3.8-4.9
 $p = c'/c = 2$

Volume of $\text{Pb}(\text{NO}_3)_2$ in ml.	Volume of the dye in ml.	Optical density of the mixture (a)	Optical density of the dye (b)	Difference in optical density (a - b)	Remarks
0	50	0.180	0.180	..	The peak of the curve occurs at a ratio of 1:1 (Fig. 3, Curve B)
5	45	0.210	0.175	0.035	
10	40	0.195	0.155	0.040	
15	35	0.185	0.140	0.045	
20	30	0.180	0.130	0.050	
25	25	0.185	0.115	0.070	
30	20	0.185	0.100	0.085	
35	15	0.175	0.075	0.100	
40	10	0.155	0.065	0.090	
45	5	0.100	0.060	0.040	

TABLE VIII

Concentration of $\text{Pb}(\text{NO}_3)_2$ (c) .. 1.0×10^{-3} M
 Concentration of the dye (c') .. 2.5×10^{-4} M
 pH of the mixtures 4.0-4.4
 $p = c'/c = 2.5$

Volume of $\text{Pb}(\text{NO}_3)_2$ in ml.	Volume of the dye in ml.	Optical density of the mixture (a)	Optical density of the dye (b)	Difference in optical density (a - b)	Remarks
0	50	0.140	0.140	..	The peak of the curve occurs at a ratio of 1:1 (Fig. 1, Curve D)
5	45	0.355	0.135	0.220	
10	40	0.360	0.120	0.240	
15	35	0.335	0.105	0.230	
20	30	0.315	0.095	0.220	
25	25	0.290	0.070	0.220	
30	20	0.250	0.065	0.185	
35	15	0.195	0.160	0.135	
40	10	0.130	0.045	0.085	
45	5	0.090	0.025	0.065	

From the observations recorded in this paper and on an examination of the curves, we find that the peaks in every case occur at a value of 0.5 for the ratio

$$\frac{[\text{Pb}^{++}]}{[\text{Pb}^{++}] + [\text{R}]}$$

where $p = 1$. Hence it is concluded that the complex has a composition of 1:1 of the reactants. (It may be noted, however, that in the figures, [] represent the volumes of the solutions and not the concentrations.) The same conclusion is also arrived at where p is not equal to one. It may further be mentioned that it was experimentally ascertained that no appreciable change in colour occurs in the dye for the small changes in the pH value which accompanied the addition of $\text{Pb}(\text{NO}_3)_2$ to Alizarin Red S.

Influence of pH on the stability of the complex.—Figure 4 represents the change in the optical density of the complex solution containing 1:1 ratio of 2.0×10^{-4} M. concentration of the reactants. The complex solution shows a variation in the region of maximum absorption, with the change of pH of the medium. It will be of interest here to compare the influence of pH on the change of colour of the complex with that of the dye itself. The changes of colour of Alizarin Red S with pH have been reported earlier.⁷ In Table IX we have compared the regions of maximum absorption of the dye and the complex at various pH values.

TABLE IX

pH	Region of maximum absorption $m\mu$	
	Dye	Complex
1.4	420	420
3.7-4.3	420	420
5.4-5.7	460	490
7.1-8.2	520	490
10.4	520	520
13.0	560	..

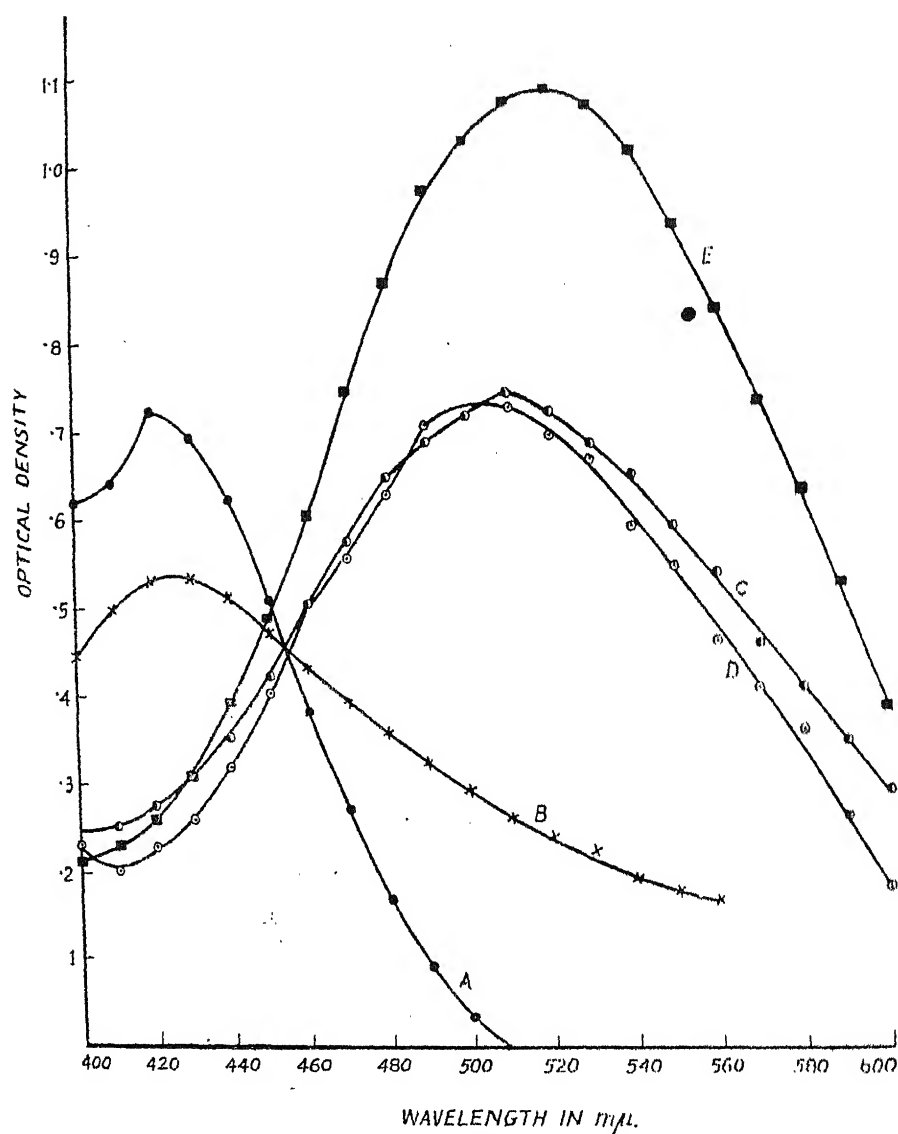


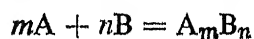
FIG. 4. Influence of pH on the absorption of lead alizarin sulphonate complex. Curve A: pH 1.4; Curve B: pH 3.7 to 4.3; Curve C: pH 5.4 to 5.7; Curve D: pH 7.1 to 8.2; Curve E: pH 10.4.

From the above table it may be seen that between the pH range 5.4–8.2 the region of maximum absorption of the complex is 490 $m\mu$ which is different from that of the dye at the same pH ranges. At other pH values the regions of maximum absorption are more or less identical in the two solutions.

This is because the complex is stable in the regions abovementioned and at other regions it is mainly the change of colour of the dye that influences the change in maximum absorption in both the solutions.

DISCUSSION

For the determination of the composition of the coloured complex Job's method of continuous variation¹⁰ has been employed using optical density as a guide of the complex formation. If we consider the formation of the complex compound in the system:



we have the value of the formation constant K as,

$$K = \frac{c_3}{c_1^m \cdot c_2^n}, \quad (1)$$

where c_1 , c_2 and c_3 represent activities \approx molar concentrations of A, B and the complex, respectively. In the continuous variation method the following restriction is imposed,

$$c_1 + c_2 = a \quad (2)$$

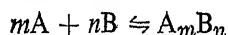
where a is a constant, it can be shown that when the concentration of A_mB_n is maximum,

$$c_2/c_1 = n/m \quad (3)$$

$$\frac{dc_3}{dc_1} = 0. \quad (4)$$

We thus conclude that for a constant total concentration of the metallic ion and complexing agent, the concentration of the complex is greatest when metal and complexing agent are present in the system in a ratio in which they exist in the complex.¹¹ If the complex is the only coloured substance present in the system, the optical density of the solution is proportional to the complex concentration. Hence, a graph showing the variation of optical density with composition of the system would give a curve with a maximum at the composition corresponding to the formula of the complex. In our case, however, the dye has an absorption in the same region as the complex, whereas lead ions do not show any absorption at the wavelength and dilution employed. Job stated that the method was not applicable to the systems in which more than one compound was formed, while Vosburgh and Cooper⁹ were able to apply the method to a special case in which they have determined the equilibria involving three chelate compounds.

The equilibrium in the reaction:



can be worked out by the following method.

If $(l - x)$ ml. of a solution of A of molar concentration c per ml. be added to x ml. of a solution of B of molar concentration c' per ml. ($c' = pc$) and if c_1 , c_2 and c_3 be the respective molar concentrations per ml. of A, B and A_mB_n after equilibrium has been attained, the following equations apply for any such mixture:

$$c_1^m \cdot c_2^n = K_d c_3 \quad (5)$$

where K_d is the dissociation constant of the complex.

$$c_1 + mc_3 = c(1 - x) \quad (6)$$

$$c_2 + nc_3 = pcx \quad (7)$$

Starting from the above equations Job showed that the equation (8) is true only for that value of x for which c_3 is maximum.

$$\frac{c^{m+n-1} \cdot p^{n-1} \{(pm + n)x - n\}^{m+n}}{m^{n-1} \cdot n^{m-1}} = K_d \{n - (m + n)x\} (p - 1)^{m+n-1} \quad (8)$$

With equimolecular solutions of A and B, ($p = 1$) the right-hand side of the equation becomes $= 0$, and hence,

$$\frac{m}{n} = \frac{l - x}{x} \quad (9)$$

as c , p , m and n are finite constants.

Hence if we determine the value of x where c_3 is maximum the formula of the complex can be obtained from the ratio m/n in the equation (9) which is identical with equation (3).

For the calculation of the formation constant we have employed the data given in the Tables I, II and III plotted in Fig. 5, where observed optical density (not the difference in optical density) has been plotted against

$$\frac{[\text{Pb}^{++}]}{[\text{Pb}^{++}] + [\text{R}]}$$

It may be assumed that in the descending portion of the curve where Pb^{++} ions are in excess most of the dye is bound up in the complex and, therefore, the optical density of the free dye does not contribute substantially to the optical

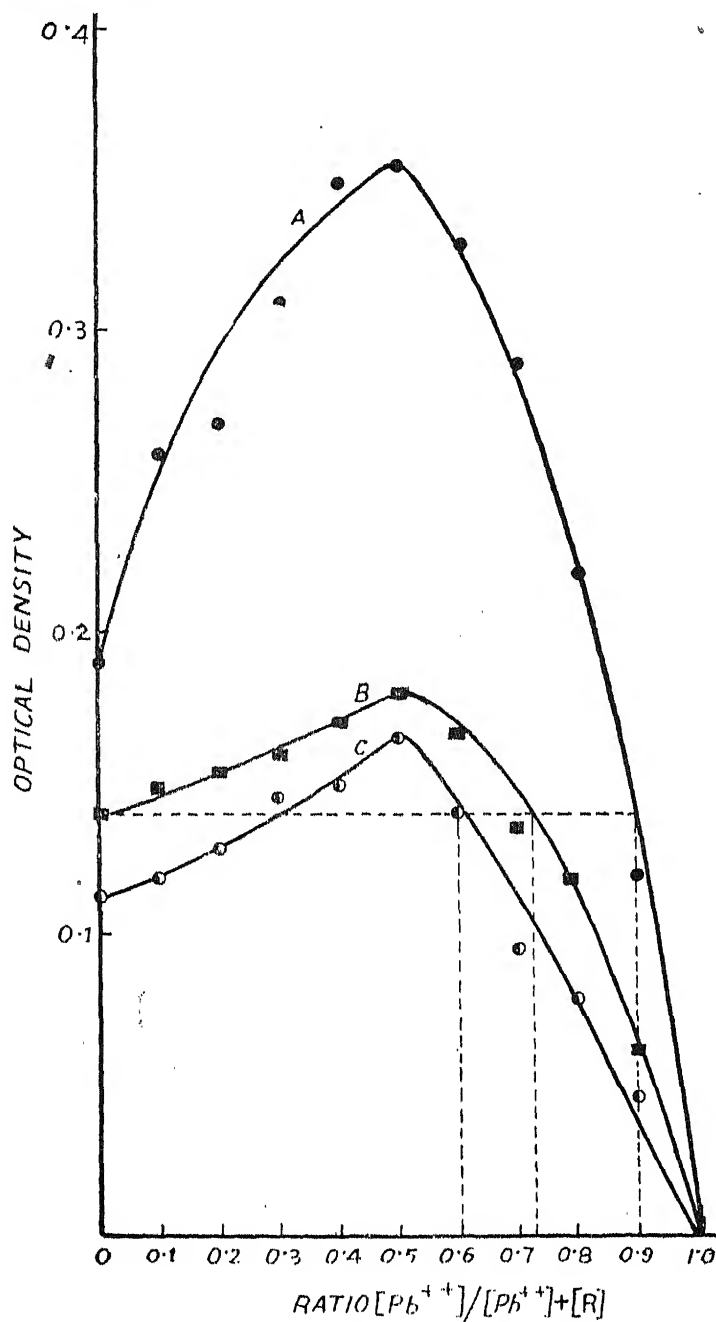
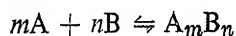


FIG. 5. Calculation of K from Absorption Spectra Data. Values of a and b have been read corresponding to the same optical density ($D = 0.14$) from the curves A, B and C.

Curve A: $c = 5 \times 10^{-4} M$, $p = 1$; Curve B: $c = 2.5 \times 10^{-4} M$, $p = 1$; Curve C: $c = 2.0 \times 10^{-4} M$, $p = 1$.

density of the system. Hence the observed optical density is mainly due to the colour of the complex. We may, therefore, assume that in curves A, B and C at the points where the optical densities are the same, the amounts of complex formed are indetical.

For the system:



where $m/n = 1$ or $m = n = 1$.

The formation constant,

$$K = \frac{x}{(a-x)(b-x)}, \quad (10)$$

where x = concentration of the complex, and a and b are the initial concentrations of $Pb(NO_3)_2$ and Alizarin Red S respectively. Taking two concentrations a_1 and a_2 and b_1 and b_2 of the reactants giving the same optical density, that is, the same values of x we have,

$$K = \frac{x}{(a_1-x)(b_1-x)} = \frac{x}{(a_2-x)(b_2-x)} \quad (11)$$

or

$$x = \frac{a_1b_1 - a_2b_2}{(a_1 + b_1) - (a_2 + b_2)} \quad (12)$$

Knowing the value of x in equation (12), the value of K can be found out by substitution in equation (10).

We have calculated the values of the formation constant (at 0.14 for the optical density) in the curves A, B and C of Fig. 5 and the average value comes out to be 5.0×10^4 .

The free energy in terms of the constant K is represented by,

$$\Delta F = -RT \log K,$$

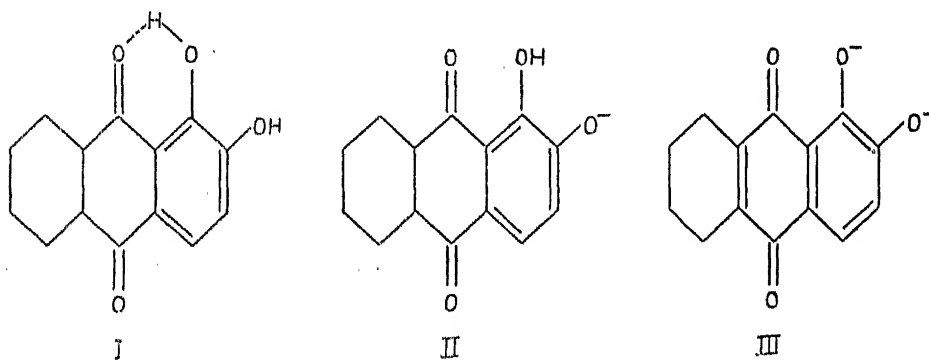
where the terms have their usual significance.

In this system the value of ΔF at a temperature 28° C. works out to be -6.4 K. calories.

It is customary to calculate the values of formation constant by "swamping" the complexing agent with simple ions in order to obtain systems of constant ionic strength. It was not possible in our case because the colour of the dye itself is susceptible to colour changes by the addition of neutral

salts like KCl, NaCl, etc. Moreover the solutions employed were extremely dilute and were of the order of 10^{-4} M.

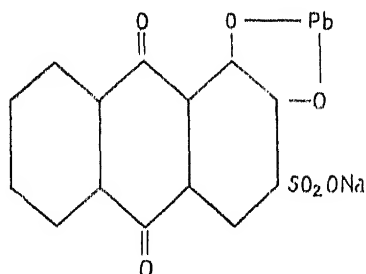
Alizarin Red S is capable of existing in three ionizable forms depending upon the pH of the medium. The alizarin molecule can be represented by the following three structures:



Since the ratio of the reactants to form the complex is 1 : 1, the value of

$$\frac{[\text{Pb}^{+2}]}{[\text{Pb}^{+2}] + [\text{R}]}$$

being = 0.5 at the peaks of the curve, the structure of the complex is likely to be:



It may be recalled that Leibhafsky and Winslow¹² also obtained evidence of the replacement of two phenolic hydrogens by bipoisitive zirconyl ion and the structure assigned by them to the complex is similar to that reported here.

REFERENCES

1. SANDELL, E. B., 1950, *Colorimetric Analysis of Traces of Metals*, Interscience, New York, p. 123.
2. B.D.H. *Book of Organic Reagents*, Poole, 1949, p. 4.
3. PARKER, C. A. AND GODDARD, H. P., 1950, *Anal. Chim. Acta*, **4**, 517.

4. VENKATESWARLU, K. S. AND RAGHAVA RAO, BH. S. V., 1956, *Ibid.*, **13**, 79.
5. SARMA, D. V. N. AND RAGHAVA RAO, BH. S. V., 1955, *Ibid.*, **13**, 142.
6. WARE, E., 1945, *U.S. Atomic Ener. Comm. Rep.*, *MDDC*, 1432.
7. MUKHERJI, A. K. AND DEY, A. K., 1957, *Proc. Nat. Acad. Sci., India*, **26 A** (forthcoming issue).
8. KUHN, H., 1948, *J. Chem. Phys.*, **16**, 840; 1949, *Ibid.*, **17**, 1198.
9. VÖSBURGH, W. C. AND COOPER, G. R., 1941, *J. Amer. Chem. Soc.*, **63**, 437.
10. JOB, P., 1928, *Comp. Rend.*, 180; 1928, *Ann. Chim.*, **9** (10), 113; 1936, *Ibid.*, **11** (6), 97.
11. MARTELL, A. E. AND CALVIN, M., 1953, *Chemistry of Metal Chelate Compounds*, Prentice Hall, New York, p. 29.
12. LEIBHAFSKY, H. A. AND WINSLOW, E. H., 1938, *J. Amer. Chem. Soc.*, **60**, 1776.

AN INVERSION FORMULA FOR THE THIRD ITERATE OF LAPLACE TRANSFORM

BY B. B. MISRA

(D.S.B. Government College, Nainital)

Received on December 28, 1955

THE triply iterated Laplace transform

$$f(x) = \int_{0+}^{\infty} e^{-xp} dp \int_{0+}^{\infty} e^{-p\sigma} d\sigma \int_0^{\infty} e^{-\sigma t} \phi(t) dt$$

has been studied by Akutowicz (1, p. 1,093) which by a formal change of the order of integration yields the L_3 -transform

$$f(x) = \int_0^{\infty} e^{xt} E(xt) \phi(t) dt \quad (A)$$

where $E(x)$ denotes the exponential integral

$$E(x) = \int_x^{\infty} e^{-t} t^{-1} dt$$

The kernel $e^{xt} E(xt)$ of this integral can be expressed as $\Psi(1, 1; xt)$ where Ψ is the confluent hypergeometric function defined by

$$\Psi(a, c; x) = \frac{1}{\Gamma(a)} \int_0^{\infty} e^{-xt} t^{a-1} (1+t)^{c-a-1} dt, \quad \operatorname{Re}(a) > 0$$

The object of this paper is to give an inversion theorem for this transform by considering it in the form

$$\int_0^{\infty} \Psi(1, 1; xt) \phi(t) dt$$

Theorem.—If (i) $f(x)$ is continuous and has derivatives of all orders in $(0, \infty)$, (ii) $\phi(t)$ is continuous in $(0, \infty)$ and

$$\begin{aligned} \phi(t) &= O(t^{\mu}), & \operatorname{Re}(\mu) > 0 & \quad (t \rightarrow 0) \\ &= O(e^{-t^{\gamma}}), & \operatorname{Re}(\gamma) > 0 & \quad (t \rightarrow \infty), \end{aligned}$$

(iii) $\int_0^{\infty} x^{p'-1} f^{(n)}(x) dx$ [$p' = \operatorname{Re}(p)$] converges absolutely, then

$$\phi(t) = \frac{1}{2\pi i} \lim_{T \rightarrow \infty} \int_{p'-iT}^{p'+iT} g(-p) t^{p-x-1} dp$$

where

$$g(-p) = \frac{(-1)^n}{\Gamma(p) \Gamma(n-p+1) \Gamma(p-n)} \int_0^\infty x^{p-1} f^{(n)}(x) dx$$

provided that $n < p' < n+1$, $\operatorname{Re}(n/2 \pm n + \mu) \geq 0$, $\operatorname{Re}(p-1-n/2 \pm n) \geq 0$; $f(x)$ and $\phi(t)$ being connected by (A).

Proof.—We know that (2, p. 258)

$$\frac{d^n}{dx^n} \{\Psi(a, c; x)\} = (-1)^n (a)_n \Psi(a+n, c+n; x)$$

Therefore we have

$$\frac{d^n}{dx^n} \{f(x)\} = (-1)^n n! \int_0^\infty \Psi(n+1, n+1; xt) t^n \phi(t) dt$$

Multiplying both the sides by x^{p-1} and integrating between 0 and ∞ we get

$$\begin{aligned} & \int_0^\infty x^{p-1} f^{(n)}(x) dx \\ &= (-1)^n n! \int_0^\infty x^{p-1} \int_0^\infty \Psi(n+1, n+1; xt) t^n \phi(t) dt dx \\ &= (-1)^n n! \int_0^\infty t^n \phi(t) \int_0^\infty \Psi(n+1, n+1; xt) x^{p-1} dx dt \\ &= (-1)^n n! \int_0^\infty t^{n-p} \phi(t) \int_0^\infty \Psi(n+1, n+1; u) u^{p-1} du dt \end{aligned}$$

on changing the order of integration and making a slight change of variable.

To justify the change in the order of integration we first note that (2, p. 264)

$$\Psi(n+1, n+1; x) = e^{x/2} \cdot x^{-(n+1)/2} W_{-(n+1)/2, n/2}(x)$$

where $W_{-(n+1)/2, n/2}(x)$ denotes Whittaker's function.

But (4, pp. 343, 346)

$$W_{k,m}(x) = O(x^{\pm m+1/2}) \text{ for small } x,$$

and

$$= O(x^k e^{-x/2}) \text{ for large } x.$$

Therefore

$$\begin{aligned}\Psi(n+1, n+1; x) &= O(x^{-n/2 \pm n}) & (x \rightarrow 0) \\ &= O(x^{-n-1}) & (x \rightarrow \infty).\end{aligned}$$

Now if

$$A(x) = x^{p-1} \int_0^\epsilon \Psi(n+1, n+1; xt) t^n \phi(t) dt$$

where ϵ is small and

$$B(t) = t^n \phi(t) \int_0^\infty \Psi(n+1, n+1; xt) x^{p-1} dx$$

we see that $A(x)$ is uniformly convergent for $x > 0$ if

$$R\left(p-1-\frac{n}{2} \pm n\right) \geq 0, \quad R\left(\frac{n}{2} \pm n + \mu + 1\right) > 0$$

and $B(t)$ is uniformly convergent for $t > 0$ if

$$R\left(\frac{n}{2} \pm n + \mu\right) \geq 0, \quad R\left(p-\frac{n}{2} \pm n\right) > 0$$

Also if we consider the integral

$$I = \int_T^\infty t^n \phi(t) dt \int_{T'}^\infty \Psi(n+1, n+1; xt) x^{p-1} dx$$

where T and T' are large we find that $|I|$ does not exceed a constant multiple of

$$\int_T^\infty |t^{-1} e^{-t^\gamma}| dt \int_{T'}^\infty |x^{p'-n-2}| dx$$

which tends to zero provided that $\operatorname{Re}(\gamma) > 0$.

Hence the order of integration can be changed under the conditions stated.

Now (2, p. 285)

$$\int_0^\infty t^{b-1} \Psi(a, c; t) dt = \frac{\Gamma(b) \Gamma(a-b) \Gamma(b-c+1)}{\Gamma(a) \Gamma(a-c+1)}$$

provided $0 < \operatorname{Re}(b) < \operatorname{Re}(a)$, $\operatorname{Re}(c) < \operatorname{Re}(b) + 1$,

Therefore

$$\begin{aligned} \int_0^{\infty} x^{p-1} f^{(n)}(x) dx \\ = (-1)^n \Gamma(p) \Gamma(n-p+1) \Gamma(p-n) \int_0^{\infty} t^{n-p} \phi(t) dt \end{aligned}$$

or

$$\begin{aligned} \int_0^{\infty} t^{n-p} \phi(t) dt \\ = \frac{(-1)^n \int_0^{\infty} x^{p-1} f^{(n)}(x) dx}{\Gamma(p) \Gamma(n-p+1) \Gamma(p-n)} = g(-p), \text{ say.} \end{aligned}$$

Since the integral $\int_0^{\infty} x^{p-1} f^{(n)}(x) dx$ converges absolutely by hypothesis and the integral $\int_0^{\infty} t^{n-p} \phi(t) dt$ also converges absolutely, applying Mellin's inversion formula (3, p. 46), we have

$$\phi(t) = \frac{1}{2\pi i} \lim_{T \rightarrow \infty} \int_{p'+iT}^{p'-iT} g(-p) t^{p-n-1} dp$$

which completes the proof of the theorem.

I am thankful to Dr. K. M. Saksena for help in the preparation of this paper.

REFERENCES

1. AKUTOWICZ, E. J., 1948, "The third iterate of Laplace transform," *Duke Mathematical Journal*, **15**, 1093-1132.
2. ERDELYI, A., 1953, (*Bateman Manuscript Project*)—*Higher Transcendental Functions*, **1**, pp. 258, 264, 285.
3. TITCHMARSH, E. C., 1937, *Theory of Fourier Integrals*.
4. WHITTAKER, E. T. AND WATSON, G. N., 1946, *Modern Analysis*.

PHYSICO-CHEMICAL STUDIES IN THE FORMATION OF TRIVALENT MANGANESE

Part I. Oxidation of Manganese II Sulphate by Potassium Dichromate.

BY DHIRENDRA NATH CHAKRAVARTY AND SATYESHWAR GHOSH

(Department of Chemistry, Allahabad University, Allahabad)

Received on July 19, 1956

ABSTRACT

The formation of manganese ion of valency greater than two by the oxidation of bivalent manganese with potassium dichromate has been studied in presence of a large excess of acid. The changes in colour have been noted by using Klett-Summerson's photoelectric colorimeter in the region 6,400–7,000 Å.U. It has been observed that the extent of oxidation is favoured by the increase in concentration of either manganous ion or of dichromate in a highly acidic medium. It has further been suggested that the mechanisms of oxidation of manganous ion either by dichromate or by permanganate are similar.

THE trivalent state of manganese is unstable and solutions can only be stabilised in presence of excess acids. The well-known salt of the series is manganic sulphate $Mn_2(SO_4)_3$,¹ which has been obtained by the interaction of a mixture of manganous sulphate and potassium permanganate, in presence of a large excess of sulphuric acid. The same compound has also been prepared by the reaction between manganous sulphate and manganese dioxide by Taube,² and was used as a catalyst in the reaction between chlorine and oxalic acid. A perusal of literature shows that in all the cases the trivalent manganese is formed by the interaction of either heptavalent or tetravalent manganese compounds with bipovalent manganese. Recently the formation of trivalent manganese compounds has been studied by Ibers and Davidson³ spectrophotometrically, by the interaction of potassium permanganate and manganous sulphate in presence of hydrochloric acid. Cabello⁴ noted the formation of a trivalent manganese complex in the reduction of an oxalate by potassium permanganate in presence of a manganous salt. Thus, all attempts so far mentioned in literature refer to the formation of a higher-valent manganese ion by the oxidation of bivalent manganese either by potassium permanganate or manganese dioxide. The present paper deals with our attempts in the study of formation of higher-valent manganese ion using potassium dichromate or chromic acid as an oxidising agent.

EXPERIMENTAL

Solutions of manganese sulphate, potassium dichromate and sulphuric acid were prepared using reagent grade chemicals in double distilled conductivity water and were standardised by the usual methods. At first a preliminary experiment was done to observe the reaction between manganous sulphate and potassium dichromate in presence of concentrated sulphuric acid. The quantity of reactants were varied and from the experiments it has been concluded that trivalent manganese is produced by the oxidation of manganous sulphate with potassium dichromate. For the detection of the formation of trivalent manganese, the changes in colour were noted using

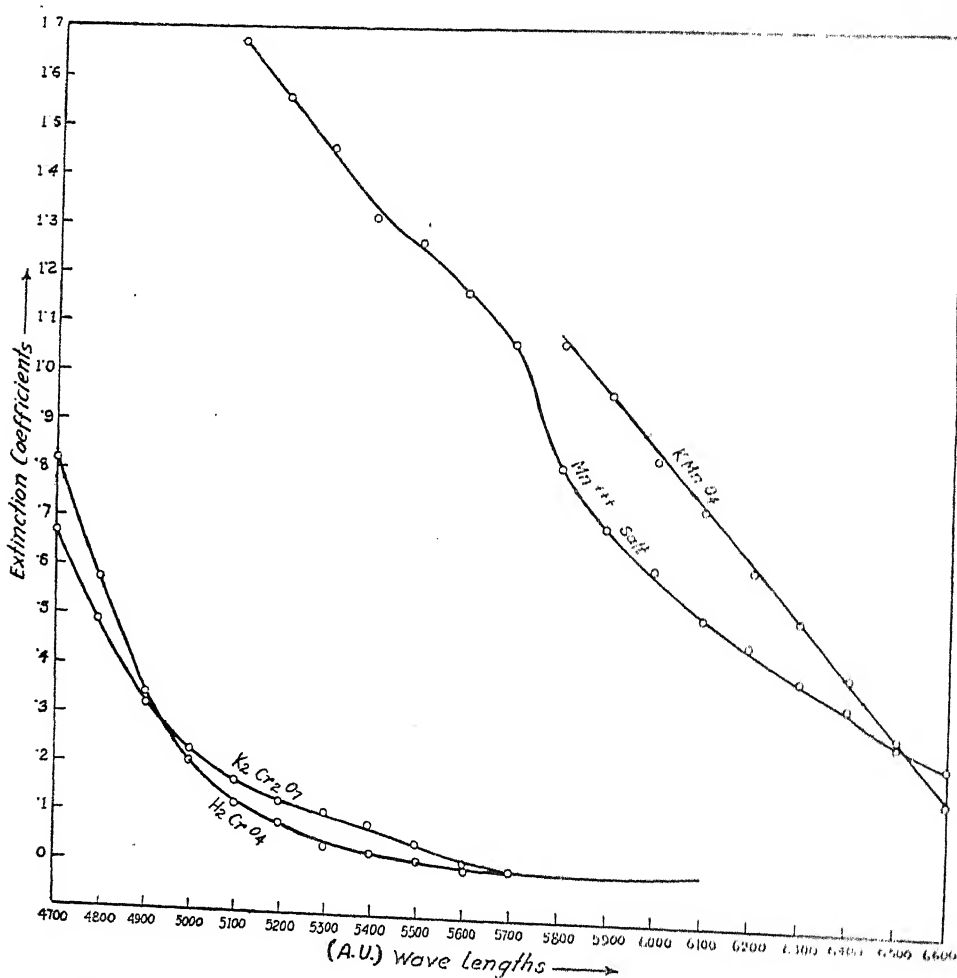


FIG. 1. Showing the variation of the extinction coefficient with the wave-length using the solutions of $KMnO_4$, $Mn_2(SO_4)_3$, $K_2Cr_2O_7$ and H_2CrO_4 .

Klett-Summerson's photoelectric colorimeter. Solutions of dichromate, permanganate, and manganese sulphate were first studied for their absorptions on an Adam-Hilger Nutting's spectrophotometer. All measurements were performed at a temperature of 25° C. From spectrophotometric measurements it was observed that potassium dichromate and chromic acid have got absorption in a spectral region lower than 5700 A.U., whereas potassium permanganate and manganese sulphate are characterised by least absorption in the visible region. A typical set of results of the measurement of the extinction coefficients with the spectrophotometer for different wavelengths for solutions of potassium dichromate, chromic acid, potassium permanganate and manganic sulphate are reproduced below:

Figure 1 shows the graphical representation of the same where the extinction coefficients are plotted against the wavelengths.

TABLE I

Wavelength A.U.	Extinction coefficient			
	K ₂ Cr ₂ O ₇ 0·0042 M	K ₂ CrO ₄ 0·0084 M	KMnO ₄ 0·005 M	Mn ₂ (SO ₄) ₈ 0·025 M
4700	0·82	0·67	Beyond scale	
4800	0·58	0·49
4900	0·34	0·32
5000	0·21	0·23	..	1·87
5100	0·12	0·17	..	1·67
5200	0·09	0·13	..	1·56
5300	0·04	0·11	..	1·46
5400	0·03	0·09	..	1·32
5500	0·02	0·05	..	1·27
5600	0·00	0·01	..	1·07
5700	..	0·00	..	0·97
5800	1·07	0·82
5900	0·97	0·70
6000	0·84	0·62
6100	0·74	0·52
6200	0·62	0·47
6300	0·52	0·40
6400	0·41	0·36
6500	0·27	0·29
6600	0·24	0·17
			Beyond visibility	

Table I shows that if a suitable filter be chosen, it would permit the transmission of light through a dichromate solution but will absorb light through

a permanganate or manganous sulphate solution. Hence Klett filter No. 66 (wavelength range between 6400 and 7000 A.U.) was chosen. As it is expected that trivalent chromium may be one of the reduced products of dichromate in the reaction mixture the extinction coefficients of a chromium sulphate solution produced by the reduction of 0.0042 M dichromate by alcohol in presence of concentrated sulphuric acid were also measured at different wavelengths. The extinction coefficient of chromium sulphate of this concentration in the region between 6400–7000 A.U. is found to be small in comparison to the extinction coefficients of trivalent manganese or potassium permanganate in the same region of observation. It may, however, be mentioned here that the concentration of chromium sulphate produced is much smaller than 0.0042 M in the reaction mixtures studied and, therefore, the effect of this salt in our measurements might be regarded as negligible. A set of experiments was performed for the measurement of absorption of light by the photoelectric colorimeter at different intervals of time and the results for the various solution systems are recorded in the following tables:—

TABLE II

Effect of varying the concentration of sulphuric acid

Manganous sulphate = 0.0025 M

Potassium dichromate = 0.00416 M

Time in minutes	Colorimeter readings		
	1.875 H ₂ SO ₄	3.75 M H ₂ SO ₄	7.5 M H ₂ SO ₄
0	7.0	13.0	25.0
1	7.5	13.5	30.0
2	7.5	14.0	32.5
3	7.5	15.0	33.0
4	7.5	15.0	34.0
5	7.5	15.0	35.0
10	8.0	15.0	35.5
15	8.0	15.0	39.0
20	8.0	15.0	40.5
25	8.0	15.0	40.5
30	8.0	15.0	41.0
40	8.0	15.0	41.5

From the above table we find that the oxidation of bivalent manganese to the trivalent stage is negligible with lower concentration of acid but is appreciable as the amount of acid is increased. In the following two tables

the results of similar sets of experiments with increasing concentrations of manganous sulphate are given:

TABLE III

Effect of varying concentration of manganous sulphate

Potassium dichromate == 0.00416 M
Sulphuric acid == 7.5 M

Time in minutes	Colorimeter readings	
	0.05 M MnSO ₄	0.005 M MnSO ₄
0	25.0	25.0
1	195.0	36.0
2	230.0	40.0
3	262.5	44.5
4	290.5	45.5
5	305.0	46.5
10	335.0	53.0
20	340.0	57.0

The results presented above show that higher valency of manganese results by the oxidation of manganese sulphate by dichromate in highly acid medium the quantity of the higher-valent compound increasing with the concentration of manganous sulphate.

TABLE IV

Effect of varying concentration of dichromate

Manganous sulphate == 0.05 M
Sulphuric acid == 7.5 M
Potassium dichromate == 0.00083 M

Time in minutes	Colorimeter readings
0	25.0
1	83.0
2	93.0
4	94.0
5	94.0
10	94.0

Comparing the above readings with the readings given in the second column of Table III we find that the extent of oxidation decreases with the concentration of dichromate. The results of the above tables are graphically represented in Fig. 2.

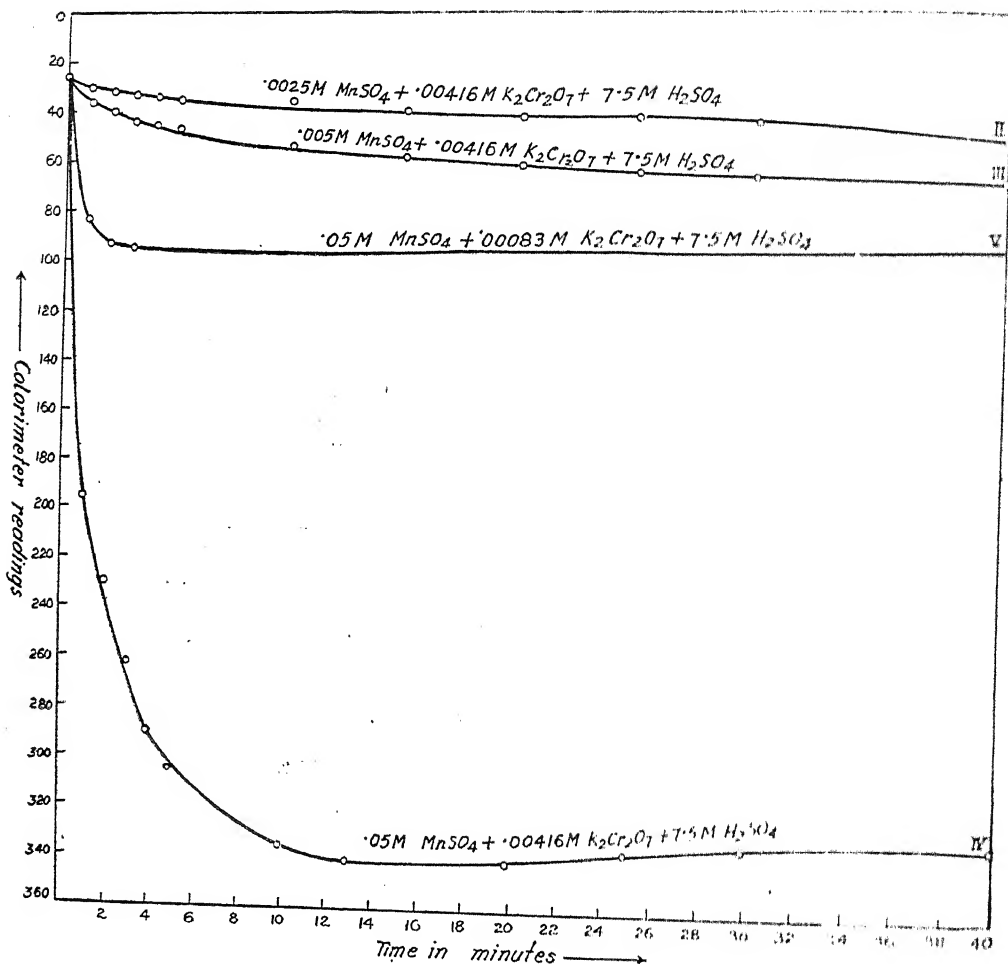


FIG. 2. The colorimeter readings have been plotted against different time intervals, for solutions containing varying amounts of manganous sulphate and potassium dichromate.

DISCUSSION

The results presented in this paper show that the oxidation of bivalent manganese can be effected by potassium dichromate in a highly acid medium. It may further be concluded that the extent of oxidation is favoured by the increase in the concentration of either manganous sulphate or of potassium

dichromate. It should however be understood clearly that the concentration of acid should be fairly large in order to observe an appreciable formation of a higher valent manganese ion.

As has been mentioned in the introductory part of this paper that all previous workers⁵⁻⁹ have obtained trivalent manganese with a compound containing manganese in a higher state of valency of the oxidation of bivalent manganese. We have now shown that the oxidation of bivalent manganese can also occur by hexavalent chromium. It was thought worthwhile to compare the oxidation action of potassium dichromate and potassium permanganate on manganous sulphate. The detail of this investigation has been reported in a separate paper.¹⁰ It was seen therefrom that at very low concentrations both dichromate and permanganate, the same amount of manganic sulphate is produced but at a higher concentration of dichromate a smaller amount of trivalent is found to be formed. Further investigations were carried out in this line by the authors and the reaction between dichromate and manganous sulphate was found to be reversible.¹¹ It therefore appears, that the mechanism of oxidation of bivalent manganese either by permanganate or by dichromate are similar excepting in the later case the reaction is a reversible one. The main factor responsible in the formation of a manganese ion of a higher valency using permanganate ion as an oxidant is its oxidising property. It does not appear to contribute itself to the formation of the trivalent manganese by its own reduction. It is necessary to report here that the permanganate solution in such a highly acid medium as 30 N sulphuric acid gradually gets decolourised showing that permanganic acid has a tendency to decompose by itself in a highly acid medium. But the results that have been presented here show that the red colour produced by the interaction of dichromate and manganous sulphate remains considerably stable. This indicates that the oxidation of manganous sulphate by potassium dichromate in highly acid medium is due to the formation of a higher-valent manganese lower than the permanganate stage.

The authors are thankful to the Ministry of Education, Government of India, for the award of a Senior Research Scholarship to one of them (D.N.C.). Their thanks are also due to Dr. Arun K. Dey for helpful discussions and keen interest taken in this work.

REFERENCES

1. MELLOR, J. W., 1932, *A Comprehensive Treatise of Inorganic and Theoretical Chemistry*, London, 12.
2. TAUBE, H., 1947, *J. Am. Chem. Soc.*, **69**, 1418.

3. IBERS, J. A., AND DAVIDSON, N., 1950, *Ibid.*, **72**, 4744.
4. CABELLOW, S., 1952, *Anales real. Soc. espan fis y. quim.*, Madrid, **48 B**, 207.
5. MEYER, J. AND SCHRAMN, W., 1926, *Zeit. anorg. Chem.*, **157**, 190.
6. ADAMON, A. W., 1951, *J. Phys. Chem.*, **55**, 293.
7. LAUNER, H. F. AND YOST, D. M., 1934, *J. Am. Chem. Soc.*, **56**, 2571.
8. PULLMAN, B., 1947, *J. Phys. Radium*, **8**, 36.
9. POLISSAR, M. J., 1935, *J. Phys. Chem.*, **39**, 1057.
10. CHAKRAVARTY, D. N. AND GHOSH, S., *Z. Phys. Chem.* (Communicated).
11. ———, *Unpublished work.*

EFFECT OF ACIDS ON THE RATE OF REACTION BETWEEN FORMIC ACID AND CHROMIC ACID— PART II

By A. V. MAHAJANI

(Department of Chemistry, University of Saugar)

Read at the Meeting of the Saugar Branch of the Academy
on August 27, 1955

THE reaction between chromic acid and formic acid was investigated by Dhar.¹ The effect of sulphuric acid on its rate was reported by him¹ and also by Snethlage.² This acid catalyses the reaction which, otherwise, is very slow at ordinary temperatures. As reported in a previous communication,³ acetic acid is a positive catalyst in this reaction. This paper deals with the effect of hydrochloric acid on the rate of this reaction.

The experimental procedure followed is the same as reported in the previous communication.³ The concentrations of formic and chromic acids were kept constant at 3.8 N and 1/15 N respectively, while that of the hydrochloric acid was varied from 0.00 to 1.60 N. In order to compare the effect of this acid with that of sulphuric acid, the same experiments were repeated taking sulphuric acid in place of hydrochloric acid at the same concentrations.

The order of the reaction with respect to chromic acid is one and it is not affected by the presence of hydrochloric acid in the system. This is shown by the data given in the following table.

TABLE I

Initial concentrations in the reaction mixture

Formic acid	..	3.8 N
Hydrochloric acid	..	0.4 N
Chromic acid	..	1/15 N
Temperature 40° C.		

Time (minutes)	Volume in ml. of 0.02322 hypo solution ($a - x$)	K (first order) calculated
0.0	14.10	..
11.5	11.98	0.01357
28.5	9.60	0.01324
47.0	7.50	0.01328
73.0	5.35	0.01318
103.0	3.60	0.01316
142.0	2.20	0.01304

The values of K (first order) for different concentrations of hydrochloric and sulphuric acids in the reaction mixture at 40°, 50° and 60° C. are given in the Table II.

TABLE II
Velocity coefficients (First order)

HCl and H ₂ SO ₄ concentrations	40° C.		50° C.		60° C.	
	K (HCl)	K (H ₂ SO ₄)	K (HCl)	K (H ₂ SO ₄)	K (HCl)	K (H ₂ SO ₄)
0.00 N	0.003335	0.003335	0.006852	0.006852	0.01342	0.01342
0.02 N	0.004158	0.003929	0.008535	0.008271	0.01701	0.01544
0.08 N	0.006680	0.005804	0.01310	0.01197	0.02561	0.02226
0.16 N	0.009761	0.008690	0.01823	0.01673	0.03248	0.03226
0.24 N	0.01163	0.01236	0.02124	0.02229	0.03727	0.04182
0.32 N	0.01285	0.01619	0.02313	0.02987	0.04030	0.05867
0.40 N	0.01330	0.01968	0.02378	0.03752	0.04318	0.07005
0.64 N	0.01441	0.03333	0.02478	0.06563	0.04361	0.1135
0.96 N	0.01465	0.05821	0.02550	0.1106	0.04463	0.1852
1.28 N	0.01565	0.07758	0.02738	0.1530	0.04870	0.2577
1.60 N	0.01592	0.1046	0.02939	0.2046	0.05545	0.3686

It is evident that the reaction rate is enhanced with the increase in the concentration of hydrochloric acid and upto the acid concentration 0.16 N its effect is greater than that of sulphuric acid. This is in agreement with the effect of the two acids in other reactions, *e.g.*, hydrolysis of esters, iodination of acetone, etc.

But on further increase of acid concentration, the velocity coefficient of the reaction in presence of sulphuric acid becomes greater than that in presence of hydrochloric acid.

In the matter of temperature coefficients the effect of the two acids is practically alike. The temperature coefficients K_{50}/K_{40} and K_{60}/K_{50} are given in Table III.

TABLE III
Temperature coefficients

HCl and H ₂ SO ₄ concentration	K ₅₀ /K ₄₀ (HCl)	K ₆₀ /K ₅₀ (HCl)	K ₅₀ /K ₄₀ (H ₂ SO ₄)	K ₆₀ /K ₅₀ (H ₂ SO ₄)
0.00 N	2.05	1.95	2.05	1.95
0.02 N	2.12	1.99	2.10	1.87
0.08 N	1.99	1.96	2.06	1.86
0.16 N	1.89	1.78	1.92	1.92
0.24 N	1.82	1.75	1.80	1.82
0.32 N	1.80	1.74	1.83	1.98
0.40 N	1.78	1.81	1.90	1.87
0.64 N	1.72	1.76	1.85	1.73
0.96 N	1.74	1.75	1.90	1.67
1.28 N	1.75	1.77	1.92	1.68
1.60 N	1.84	1.88	1.95	1.80

Measurements of the percentage transmittance of aqueous solutions containing chromic acid only and chromic acid with hydrochloric and sulphuric acids (separately) were made and the observations are shown in Table IV given below. It is seen that in the range 580–530 m μ the transmittance of the solution containing sulphuric acid is slightly greater than that of the solution containing hydrochloric acid. But they are of the same order and either of them is less than the transmittance of the solution containing chromic acid only. This is apparently due to the shift in the equilibrium involving various chromate ions, the shift due to the hydrochloric acid being greater than that due to sulphuric acid. While the shift in the equilibrium by the addition of an acid can account for increase in the reaction rate, it does not appear to be the only reason, otherwise in this case hydrochloric acid should have been more effective in increasing the reaction rate than sulphuric acid at all acid concentrations.

The rate of this reaction is enhanced by hydrogen ions. A sodium formate solution cannot, noticeably, be oxidised by chromic acid in the absence of any other acid. Potassium dichromate solution can oxidise formic acid, although it is slightly less active than chromic acid at the same concentration. From these observations it is evident that it is the formic acid molecule and not the formate ion which reacts with chromate ions and hydrogen-ions have a definite role in the mechanism of the reaction. But from a study of the effect of hydrochloric acid in this reaction and its comparison with that of sulphuric acid it appears that only the hydrogen-ions supplying property of an acid cannot account for its role in this reaction.

TABLE IV

% Transmittance by chromic acid solutions

Wave-length m μ	%T Chromic acid N/15	%T Chromic acid N/15 + HCl 0.16 N	%T Chromic acid N/15 + HCl 1.6 N	%T Chromic acid N/15 + H ₂ SO ₄ 0.16 N	%T Chromic acid N/15 + H ₂ SO ₄ 1.6 N
600	100	100	100	100	100
580	99.8	99.8	98.6	100	98.8
560	96.2	95.7	92.0	96.3	91.6
550	90.1	88.9	80.5	89.3	80.8
540	78.1	75.8	63.2	76.8	63.8
530	57.0	54.1	40.2	55.2	40.8
520	32.0	29.5	20.2	30.6	20.6
510	13.3	12.5	8.3	12.9	8.38
500	3.97	3.60	2.50	3.60	2.40
490	0.73	0.66	0.50	0.66	0.52
480
470
460

It may be pointed out further work in this connection as well as work on the oxidation of glucose and glycerol is in progress.

Grateful thanks are due to Dr. A. K. Bhattacharya, Head of the Chemistry Department, and the University of Saugar for research facilities.

REFERENCES

1. DHAR, N. R., 1917, *J.C.S.*, **111**, 707.
2. SNETHLAGE, H. C. S., 1941, *Rec. Trans. Chim.*, **60**, 877.
3. MAHAJANI AND BHATTACHARYA, *Proc. Natl. Acad. Sci., India*, **23 A**, 65 (1954).

COMPARATIVE STUDY OF THE ACTIVATION OF PAPAIN BY BISULPHITE AND AMMONIUM IONS

BY RAMESH CHANDRA SINHA AND KRISHNA BAHADUR

(*Chemical Laboratories, University of Allahabad, Allahabad*)

Read on September 20, 1956

HOOPER AND KOKES¹ have observed that the optimal pH for the initial rate of papain digestion of casein is at pH 7 but the hydrolysis is much more extensive at pH 5. It is capable of hydrolysing a number of native proteins.²⁻⁷ Enzymes, which help in lowering the energy of activation of the reaction, have been found to have their activity increased by the addition of various chemicals. Several activators containing sulfhydryl, disulphide, cyanide,⁸ thiosulphate,⁹ Urea¹⁰ and amino groups¹⁰ have been found to increase the proteolytic property of papain. In the presence of sodium bisulphite at pH 6.7 papain also hydrolyses wool keratin.¹¹ The activation of papain by these activators is of two types because some of the activators have strong electron attracting groups as amino group and some of them have strong electron repelling groups as cyanide group. Hence one type of activators influence the electron repelling group and the other type of activators influence the electron attracting groups of the substrate or papain protein.¹²

We have observed in the hydrolysis of casein by papain that bisulphite and ammonium ions act as activators and the different conditions of concentration of substrate, enzyme and activators changes the nature of activation in the case of almost all the actions studied. Here a detailed description of this work is given.

EXPERIMENTAL

Substrate.—Weighed quantity of casein was taken in 25 ml. of carbon dioxide-free distilled water and heated to boiling. To this was added a drop or two of phenolphthalein and quantitative amount of .1 N caustic potash solution to afford an almost uniform solution. The quantity of KOH was so adjusted that the solution was of just pink colour. On cooling, the solution was transferred to a 100 c.c. measuring flask and the total volume was made up to 100 c.c.

Enzyme.—Papain²⁰ solution was made by dissolving weighed quantity of the enzyme in distilled water.

Digestion.—This was carried out with the casein substrate at 50° C. and pH value 5.0 (approx.) in an incubator. 10 ml. of the substrate were taken

in each of the six different 100 c.c. conical flasks and treated with 10 ml. of enzyme preparations. Weighed quantities of sodium cyanide, urea, sodium hydrogen sulphite, sodium thiosulphate and ammonium sulphate were added as activators to each of the five conical flasks except the first, which was kept as control. The final volume of the digestion mixtures was adjusted approximately to 50 ml. by adding distilled water. These flasks were then placed in the incubator and were shaken occasionally. The rate of digestion was followed up to 24 hours. From time to time 5 ml. of the filtered digestion mixture were taken out and titrated against standard potassium hydroxide solution.

The method employed for the titration of amino acids using formaldehyde was similar to the one suggested by Kolthoff and Stenger.²¹ For this a neutralised sample corresponding to about 25 c.c. of 0.1 N amino acids, 5.0 c.c. of 37% formaldehyde previously neutralised to phenolphthalein were added. The titration was done with N/41 alkali employing a standard micro burette until the colours with this indicator appeared distinctly rose red.

OBSERVATION

The results of the hydrolysis of casein by papain activated by sodium cyanide, urea, sodium thiosulphate, sodium hydrogen sulphite, ammonium sulphate and under control conditions are tabulated below.

The readings in the following tables are in terms of c.c. of N/41 potassium hydroxide solution required to neutralise the amount of liberated-COOH group in the 5 c.c. of the digestion mixture. In the beginning the pH of all the reaction media was adjusted to about 5.0° and the reaction was performed at 50° C.

DISCUSSION

As indicated by the above tables sodium bisulphate and ammonium sulphate act as activators in the proteolytic activity of papain. It is interesting to note that the activation of the enzyme by these and other activators as sodium cyanide, urea and sodium thiosulphate is very much influenced by the change of concentration of the substrate (Table I), enzyme (Table II) or the activators (Table III). Formerly it was believed that the increase in activity could be explained upon the basis of a promotor or auxo effect.¹³ However, it is very probable that in many instances the activation of an enzyme by an added substance is to be explained as due to the removal of some poison which is taken away from the enzyme because it has a greater affinity for that. Bersin,¹⁴ Hellerman^{15, 16} and others have proposed that certain enzymes are sulphhydryl compounds which are easily oxidised and which

TABLE I

Effect of substrate concentration on the activation by various compounds employing 0.5% enzyme solution, 0.5 gm. of the activator and the casein solution

Activators	5% Casein solution			1% Casein solution			2% Casein solution		
	Digestion period			Digestion period			Digestion period		
	2 hrs.	4 hrs.	24 hrs.	2 hrs.	4 hrs.	24 hrs.	1 hr.	3 hrs.	24 hrs.
Control	.. 0.33	0.35	0.45	0.24	0.34	0.68	0.22	0.32	0.38
NaCN	.. 0.23	0.45	0.63	0.43	0.58	0.82	0.57	1.28	2.32
Urea	.. 0.20	0.34	0.61	0.29	0.35	0.96	0.40	0.60	0.93
NaHSO ₃	.. 0.13	0.29	0.64	0.67	0.79	1.10	0.18	0.38	2.18
Na ₂ S ₂ O ₃	.. 0.34	0.45	0.63	0.67	0.77	1.14	0.24	0.80	2.51
(NH ₄) ₂ SO ₄	.. 0.15	0.21	1.12	0.36	0.50	1.12	0.29	0.51	1.20

TABLE II

Effect of enzyme concentration on the activation by various compounds employing 1% casein solution, 0.5 gm. of the activators and the enzyme solution

Activators	25% Papain solution			5% Papain solution			1% Papain solution		
	Digestion period			Digestion period			Digestion period		
	2 hrs.	4 hrs.	24 hrs.	2 hrs.	4 hrs.	24 hrs.	2 hrs.	4 hrs.	24 hrs.
Control	.. 0.16	0.16	0.28	0.24	0.34	0.68	0.66	0.82	1.06
NaCN	.. 0.40	0.70	1.06	0.43	0.58	0.82	0.86	0.98	1.32
Urea	.. 0.10	0.12	0.32	0.29	0.35	0.96	0.66	0.76	1.14
NaHSO ₃	.. 0.26	0.56	1.04	0.67	0.79	1.10	0.70	0.98	1.54
Na ₂ S ₂ O ₃	.. 0.30	0.66	1.14	0.67	0.77	1.14	0.86	0.96	1.36
(NH ₄) ₂ SO ₄	.. 0.20	0.22	0.96	0.36	0.50	1.12	0.54	0.70	1.68

TABLE III

Effect of concentration of the activators on the activation employing 1% casein solution, .5% enzyme solution and the activator

Activators	.025 gm. Activator			.05 gm. Activator			.1 gm. Activator		
	Digestion period			Digestion period			Digestion period		
	2 hrs.	4 hrs.	24 hrs.	2 hrs.	4 hrs.	24 hrs.	2 hrs.	4 hrs.	24 hrs.
Control	.. 0.70	0.90	0.98	0.24	0.34	0.68	0.10	0.36	0.62
NaCN	.. 0.80	1.04	1.48	0.43	0.58	0.82	0.26	0.66	1.06
Urea	.. 0.28	0.28	0.78	0.29	0.35	0.96	0.40	0.60	0.90
NaHSO ₃	.. 0.60	1.00	1.60	0.67	0.79	1.10	0.12	0.50	1.22
Na ₂ S ₂ O ₃	.. 0.76	1.08	2.02	0.67	0.77	1.14	0.40	0.70	1.10
(NH ₄) ₂ SO ₄	.. 0.30	0.30	1.80	0.36	0.50	1.12	0.42	0.74	1.74

require reducing agents for their activity. But Fruton and Bergmann¹⁷ are opposed to the theory that papain is activated by reduction inactivated by oxidation. They believe that the activator acts as a coenzyme. According to Nord this effect is due to decrease in the particle size and a consequent increase in the surface of the enzymes involved.^{18, 19} Although various theories have been put forward but even then the mechanism of activation is far from clear.

SUMMARY

It has been observed that ammonium sulphate and sodium hydrogen sulphite act as activators for the proteolytic properties of papain. These activators under certain conditions behave as stronger activating agents than sodium cyanide, sodium thiosulphate and urea. Different conditions of concentration of substrate, enzyme and activators have been studied and it has been found that under certain conditions as indicated in the Table III ammonium sulphate acts as a very good activator whereas under the same conditions urea does not show much activation.

REFERENCES

1. HOOVER, S. R. AND KOKES, E. L. C., 1942, *J. Biol. Chem.*, **144**, 161.
2. OREKHOVICH, V. N. *et al.*, 1947, *Akad., Nank, U.S.S.R.*, **57**, 475-77.

3. CHERBULIEZ, E. AND BANDET, P., 1950, *Univ. Geneva, Switz., Hebr. Chem. Acta*, **33**, 1673-88.
4. GANAPATHY, C. V. AND SASTRI, B. N., 1939, *Biochem. J.*, **33**, 1174-79.
5. RICE, R. C. *et al.*, 1945, *J. Biol. Chem.*, **158**, 609-17.
6. HOOVER, S. R. AND KOKES, E. L. C., 1947, *Ibid.*, **167**, 199-207.
7. SOMORODINCER, J. A. AND SINGHLOV, V. P., 1941, *Compt. Rend. Acad. Sci., U.S.S.R.*, **33**, 70-72.
8. SCOTT, E. M. AND SANDSTROM, W. H., 1942, *Arch. Biochem.*, **1**, 103-09.
9. RAY, N., 1946, *J. Indian Chem. Soc.*, **23**, 313-14.
10. RICE, R. C., BALLON, G. A., BOYER, P. D., LUCK, J. M. AND LUM, F. G., 1945, *J. Biol. Chem.*, **158**, 609-17.
11. MIDDLEBROOK, W. R. AND PHILLIPS, H. J., 1941, *Soc. Dyers Colourists*, **57**, 137.
12. HELLERMAN, L., 1929, *Cold Spring Harbour Symposia Quant. Biol.*, **7**, 165.
13. JAMES B. SUMNER AND FRED SOMERS, G., *Chemistry and Methods of Enzyme*, Academic Press Inc., Publishers, New York, N.Y., Third Edition, 1951 p. 23.
14. BERSIN, T., 1935, *Ergeb. Enzymforsch.*, **4**, 68.
15. HELLERMAN, L., 1937, *Physiol. Rvs.*, **17**, 454.
16. —, 1939, *Cold Spring Harbour Symposia Quant. Biol.*, **7**, 165.
17. FRUTON, J. S. AND BERGMANN, M., 1940, *J. Biol. Chem.*, **133**, 153.
18. HOLZAPPEL, L. AND NORD, F. F., 1938, *Ber.*, **71**, 1212; 1940-41, *Biodynamica*, **3**, 57.
19. NORD, F. F., 1936, *Naturwissenschaften*, **24**, 481.
20. PAPAIN, B. P. C, 1954, *A-Constantive and C-Fauria, Socilita per I 'Industria di Prodotti, Biochemicci*.
21. KOLTHOFF AND STENGER, 1947, *Volumetric Analysis*, Part II, Inter Science, p. 160.

SUPERPOSABLE FLOWS OF THE TYPE

$$\text{CURL } \mathbf{q}_1 = \lambda_2 \mathbf{q}_2 \text{ AND } \text{CURL } \mathbf{q}_2 = \lambda_1 \mathbf{q}_1$$

BY C. D. GHILDYAL

(Department of Mathematics, Lucknow University)

Received on December 10, 1956

IN 1940, Ballabh defined superposability. According to him two flows (u_1, v_1, w_1, p_1) and (u_2, v_2, w_2, p_2) are said to be superposable if a pressure $(p_1 + p_2 + \pi)$ can be determined so that the fluid moves with the velocity $(u_1 + u_2, v_1 + v_2, w_1 + w_2)$ under the external forces $(X_1 + X_2, Y_1 + Y_2, Z_1 + Z_2)$ and the pressure $(p_1 + p_2 + \pi)$ with necessary modifications in the initial and boundary conditions. By defining superposability in this manner he obtained the general conditions of superposition of two given flows.

The conditions symbolically can be written as

$$\mathbf{q}_1 \times \text{curl } \mathbf{q}_2 + \mathbf{q}_2 \times \text{curl } \mathbf{q}_1 = \text{grad } X' \quad (1)$$

where \mathbf{q}_1 and \mathbf{q}_2 are velocity vectors of the two flows and X' is a scalar function of x, y, z and t .

He also obtained an expression for π which can be written as

$$\frac{\pi}{\rho} + \mathbf{q}_1 \cdot \mathbf{q}_2 + X' = \text{constant}. \quad (2)$$

If the external forces are conservative condition (1) is still true when the force potential has the same value in each case.

From equation (1) Ballabh deduced two particular solutions which symbolically can be written as

$$\text{curl } \mathbf{q}_1 = \lambda \mathbf{q}_1 \quad \text{and} \quad \text{curl } \mathbf{q}_2 = \lambda \mathbf{q}_2 \quad (3)$$

$$\text{curl } \mathbf{q}_1 = \lambda_2 \mathbf{q}_2 \quad \text{and} \quad \text{curl } \mathbf{q}_2 = \lambda_1 \mathbf{q}_1 \quad (4)$$

In the first case the vortex lines of the flows coincide with their own stream lines. In the second case the vortex lines of one flow coincide with the stream lines of the other and *vice versa*.

In this paper the second particular case of superposability is discussed and certain new results have been obtained.

In 1943, Ballabh obtained certain results by taking λ_1 and λ_2 both independent of space variables and time.

From equation of continuity, we have

$$\text{div } \mathbf{q}_1 = 0 \quad \text{and} \quad \text{div } \mathbf{q}_2 = 0 \quad (5)$$

for the first and second flow respectively.

From equations (4) and (5) we get

$$-\nabla^2 \mathbf{q}_1 = \nabla \lambda_2 \times \mathbf{q}_2 + \lambda_1 \lambda_2 \mathbf{q}_1 \quad (6)$$

$$-\nabla^2 \mathbf{q}_2 = \nabla \lambda_1 \times \mathbf{q}_1 + \lambda_1 \lambda_2 \mathbf{q}_2 \quad (7)$$

Also from equation (4), we have

$$\left. \begin{aligned} \nabla \lambda_1 \cdot \mathbf{q}_1 &= 0 & (i) \\ \nabla \lambda_2 \cdot \mathbf{q}_2 &= 0 & (ii) \end{aligned} \right\} \quad (8)$$

From equation (8) (i) we conclude that the stream lines of the flow (u_1, v_1, w_1) and vortex lines of the flow (u_2, v_2, w_2) lie on the surfaces $\lambda_1 = \text{constant}$. Similarly from (8) (ii) the stream lines of (u_2, v_2, w_2) and vortex lines of (u_1, v_1, w_1) lie on the surfaces $\lambda_2 = \text{constant}$.

The equations of motion of a viscous homogeneous incompressible fluid can be written as

$$\frac{\partial \mathbf{q}}{\partial t} = \mathbf{q} \times \text{curl } \mathbf{q} - \text{grad } \chi + \nu \nabla^2 \mathbf{q} \quad (9)$$

where the symbols have their usual meanings.

Hence the equations of motion for \mathbf{q}_1 and \mathbf{q}_2 can be written as

$$\frac{\partial \mathbf{q}_1}{\partial t} = \lambda_2 \mathbf{q}_1 \times \mathbf{q}_2 - \text{grad } \chi_1 + \nu \nabla^2 \mathbf{q}_1 \quad (10)$$

$$\frac{\partial \mathbf{q}_2}{\partial t} = \lambda_1 \mathbf{q}_2 \times \mathbf{q}_1 - \text{grad } \chi_2 + \nu \nabla^2 \mathbf{q}_2 \quad (11)$$

It is easy to see from these that the steady motion of an ideal liquid is self-superposable.

2. Let the two flows be orthogonal, then we have

$$\mathbf{q}_1 \cdot \mathbf{q}_2 = 0. \quad (12)$$

From equation (10) under the condition given above we have,

$$\mathbf{q}_2 \cdot \frac{\partial \mathbf{q}_1}{\partial t} = \lambda_2 \mathbf{q}_2 \cdot \mathbf{q}_1 \times \mathbf{q}_2 - \mathbf{q}_2 \cdot \text{grad } \chi_1 + \nu \mathbf{q}_2 \cdot \nabla^2 \mathbf{q}_1$$

In case of steady motion, we have

$$\mathbf{q}_2 \cdot \text{grad } \chi_1 = 0 \quad (13)$$

similarly

$$\mathbf{q}_1 \cdot \text{grad } \chi_2 = 0. \quad (14)$$

The surfaces $\chi_1 = \text{constant}$ contain the stream lines of the motion (u_2, v_2, w_2) and vortex lines of the motion (u_1, v_1, w_1) . The surfaces $\chi_2 = \text{constant}$ contain stream lines of the motion (u_1, v_1, w_1) and vortex lines of (u_2, v_2, w_2) .

Hence we have

$$\chi_1 = f_2(\lambda_2) \quad \text{and} \quad \chi_2 = f_1(\lambda_1). \quad (15)$$

It is easy to notice that the surfaces $\chi_1 = \text{constant}$ and $\chi_2 = \text{constant}$ are orthogonal in this case.

3. If the liquid is non-viscous, the equations of motions reduce to

$$\frac{\partial \mathbf{q}_1}{\partial t} = \lambda_2 \mathbf{q}_1 \times \mathbf{q}_2 - \text{grad } \chi_1 \quad (16)$$

$$\frac{\partial \mathbf{q}_2}{\partial t} = \lambda_1 \mathbf{q}_2 \times \mathbf{q}_1 - \text{grad } \chi_2 \quad (17)$$

If the flows are steady, we have

$$\begin{aligned} \mathbf{q}_1 \cdot \text{grad } \chi_1 &= 0 & \text{and} & & \mathbf{q}_2 \cdot \text{grad } \chi_1 &= 0 & \text{(i)} \\ \mathbf{q}_1 \cdot \text{grad } \chi_2 &= 0 & \text{and} & & \mathbf{q}_2 \cdot \text{grad } \chi_2 &= 0 & \text{(ii)} \end{aligned} \quad (18)$$

From equations (8) and (18) we get, $\lambda_2 = f(\lambda_1)$. Hence when the liquid is non-viscous and the motions are steady, a functional relation exists between λ_2 and λ_1 .

4. Let λ_1 and λ_2 be functions of time only.* Let also $w_1 = w_2 = 0$. The equations (4) can then be written as

$$\begin{aligned} -\frac{\partial v_1}{\partial z} &= \lambda_2 u_2; \quad \frac{\partial u_1}{\partial z} = \lambda_2 v_2; \quad \frac{\partial v_1}{\partial x} - \frac{\partial u_1}{\partial y} = 0 & \text{(i)} \\ -\frac{\partial v_2}{\partial z} &= \lambda_1 u_1; \quad \frac{\partial u_2}{\partial z} = \lambda_1 v_1; \quad \frac{\partial v_2}{\partial x} - \frac{\partial u_2}{\partial y} = 0 & \text{(ii)} \end{aligned} \quad (19)$$

The equations of continuity for the two motions now reduce to

$$\frac{\partial u_1}{\partial x} + \frac{\partial v_1}{\partial y} = 0; \quad \frac{\partial u_2}{\partial x} + \frac{\partial v_2}{\partial y} = 0.$$

* Ballabh had assumed λ_1 and λ_2 to be absolute constants,

Solving equations (19), we get

$$u_1 = A_1 \sin kz + A_2 \cos kz$$

$$v_1 = A_3 \sin kz + A_4 \cos kz$$

$$u_2 = \left(\frac{\lambda_1}{\lambda_2}\right)^{\frac{1}{2}} [A_4 \sin kz - A_3 \cos kz],$$

$$v_2 = \left(\frac{\lambda_1}{\lambda_2}\right)^{\frac{1}{2}} [A_1 \cos kz - A_2 \sin kz].$$

where $k = \sqrt{\lambda_1 \lambda_2}$ = a function of time only. The A's are functions of x , y and t and satisfy the equations

$$\frac{\partial A_1}{\partial x} + \frac{\partial A_3}{\partial y} = 0; \quad \frac{\partial A_2}{\partial x} + \frac{\partial A_4}{\partial y} = 0; \quad \frac{\partial A_1}{\partial y} - \frac{\partial A_3}{\partial x} = 0;$$

$$\frac{\partial A_2}{\partial y} - \frac{\partial A_4}{\partial x} = 0.$$

The equations of motions reduce to

$$\left. \begin{aligned} \frac{\partial u_1}{\partial t} + \nu \lambda_1 \lambda_2 u_1 &= -\frac{\partial \chi_1}{\partial x} \\ \frac{\partial v_1}{\partial t} + \nu \lambda_1 \lambda_2 v_1 &= -\frac{\partial \chi_1}{\partial y} \\ \lambda_2 (v_1 u_2 - u_1 v_2) &= -\frac{\partial \chi_1}{\partial z} \end{aligned} \right\}. \quad (21)$$

$$\left. \begin{aligned} \frac{\partial u_2}{\partial t} + \nu \lambda_1 \lambda_2 u_2 &= -\frac{\partial \chi_2}{\partial x} \\ \frac{\partial v_2}{\partial t} + \nu \lambda_1 \lambda_2 v_2 &= -\frac{\partial \chi_2}{\partial y} \\ \lambda_1 (v_2 u_1 - u_2 v_1) &= -\frac{\partial \chi_2}{\partial z} \end{aligned} \right\}. \quad (22)$$

From equations (21) and (22) we get

$$\frac{\partial}{\partial z} (\lambda_1 \chi_1 + \lambda_2 \chi_2) = 0. \quad (23)$$

From equation (23) it follows that the expression $(\lambda_1 \chi_1 + \lambda_2 \chi_2)$ is independent of z . Also from (21) and (22) we get,

$$\lambda_1 \frac{\partial u_1}{\partial t} + \lambda_2 \frac{\partial u_2}{\partial t} + \nu k^2 (\lambda_1 u_1 + \lambda_2 u_2) = -\frac{\partial}{\partial x} (\lambda_1 \chi_1 + \lambda_2 \chi_2) \quad (24)$$

and

$$\lambda_1 \frac{\partial v_1}{\partial t} + \lambda_2 \frac{\partial v_2}{\partial t} + \nu k^2 (\lambda_1 v_1 + \lambda_2 v_2) = \frac{\partial}{\partial y} (\lambda_1 X_1 + \lambda_2 X_2) \quad (25)$$

Differentiating the equations (25) and (24) with respect to z we get

$$\lambda_1 \frac{\partial}{\partial t} (\lambda_2 u_2) + \lambda_2 \frac{\partial}{\partial t} (\lambda_1 u_1) + \nu k^4 (u_1 + u_2) = 0 \quad (26)$$

$$\lambda_1 \frac{\partial}{\partial t} (\lambda_2 v_2) + \lambda_2 \frac{\partial}{\partial t} (\lambda_1 v_1) + \nu k^4 (v_1 + v_2) = 0 \quad (27)$$

The condition of integrability for the motion (u_1, v_1, w_1) can be written as

$$\left(\frac{\partial}{\partial t} + \nu k^2 \right) \frac{\partial u_1}{\partial z} = \lambda_2 \frac{\partial}{\partial x} (v_1 u_2 - v_2 u_1) \quad (28)$$

and

$$\left(\frac{\partial}{\partial t} + \nu k^2 \right) \frac{\partial v_1}{\partial z} = \lambda_2 \frac{\partial}{\partial y} (v_1 u_2 - v_2 u_1) \quad (29)$$

Similarly we can get the conditions of integrability for the motion (u_2, v_2, w_2) from the equation (22).

Substituting the value of u_1, v_1, u_2 and v_2 from (20) in (28) and (29) we get, respectively

$$\begin{aligned} & \left(\frac{\partial}{\partial t} + \nu k^2 \right) \{k (A_1 \cos kz - A_2 \sin kz)\} \\ &= k \frac{\partial}{\partial x} \{(A_2^2 + A_4^2 - A_1^2 - A_3^2) \frac{1}{2} \sin 2kz \\ & \quad - (A_1 A_2 + A_3 A_4) \cos 2kz\} \end{aligned} \quad (30)$$

and

$$\begin{aligned} & \left(\frac{\partial}{\partial t} + \nu k^2 \right) \{k (A_3 \cos kz - A_4 \sin kz)\} \\ &= k \frac{\partial}{\partial y} \{(A_2^2 + A_4^2 - A_1^2 - A_3^2) \frac{1}{2} \sin 2kz \\ & \quad - (A_1 A_2 + A_3 A_4) \cos 2kz\} \end{aligned} \quad (31)$$

Equating the coefficients of $\cos kz$, $\sin kz$, $\sin 2kz$ and $\cos 2kz$ to zero, in (30) and (31) we get

$$\left. \begin{aligned} \frac{\partial (kA_1)}{\partial t} + \nu k^3 A_1 - zA_2 k \frac{\partial k}{\partial t} &= 0 \\ \frac{\partial (kA_2)}{\partial t} + \nu k^3 A_2 + zA_1 k \frac{\partial k}{\partial t} &= 0 \end{aligned} \right\} \quad \begin{matrix} \text{(i)} \\ \text{(ii)} \end{matrix} \quad (32)$$

$$\frac{\partial}{\partial x} (A_2^2 + A_4^2 - A_1^2 - A_3^2) = 0$$

and

$$\frac{\partial}{\partial x} (A_1 A_2 + A_3 A_4) = 0$$

and

$$\left. \begin{aligned} \frac{\partial (kA_3)}{\partial t} + \nu k^3 A_3 - zA_4 k \frac{\partial k}{\partial t} &= 0 \\ \frac{\partial (kA_4)}{\partial t} + \nu k^3 A_4 + zA_3 k \frac{\partial k}{\partial t} &= 0 \end{aligned} \right\} \quad \begin{matrix} \text{(i)} \\ \text{(ii)} \end{matrix} \quad (33)$$

$$\frac{\partial}{\partial y} (A_2^2 + A_4^2 - A_1^2 - A_3^2) = 0$$

and

$$\frac{\partial}{\partial y} (A_1 A_2 + A_3 A_4) = 0.$$

From equations (32) and (33) we get

$$\left. \begin{aligned} k \frac{\partial k}{\partial t} A_r &= 0 \\ \frac{\partial (kA_r)}{\partial t} + \nu k^3 A_r &= 0 \end{aligned} \right\} \text{ where } r = 1, 2, 3, 4. \quad (34)$$

This means that $\partial k / \partial t = 0$, i.e., k is independent of time, for otherwise we get $k = 0$, which is trivial, so that $\lambda_1 \lambda_2 = a^2$, an absolute constant.

Equations (34) give

$$\begin{aligned} A_1 &= \theta_x e^{-\nu a^2 t} & A_3 &= \theta_y e^{-\nu a^2 t} \\ A_2 &= \phi_x e^{-\nu a^2 t} & A_4 &= \phi_y e^{-\nu a^2 t} \end{aligned}$$

Equation (20) can now be written as

$$\left. \begin{aligned} u_1 &= (\theta_x \sin az + \phi_x \cos az) e^{-\nu a^2 t} \\ v_1 &= (\theta_y \sin az + \phi_y \cos az) e^{-\nu a^2 t} \\ w_1 &= 0 \end{aligned} \right\} \quad (35)$$

$$\left. \begin{aligned} u_2 &= \frac{\lambda_1}{a} (\phi_y \sin az - \theta_y \cos az) e^{-\nu a^2 t} \\ v_2 &= \frac{\lambda_1}{a} (\theta_x \cos az - \phi_x \sin az) e^{-\nu a^2 t} \\ w_2 &= 0 \end{aligned} \right\} \quad (36)$$

where λ_1 is a function of time only. Putting $\lambda_2 = a^2/\lambda_1$ and substituting the values of u_1 and u_2 from (35) and (36) in (26) we get

$$\begin{aligned} & \lambda_1 \frac{\partial}{\partial t} \left[\frac{a^2}{\lambda_1} (\phi_y \sin az - \theta_y \cos az) \frac{\lambda_1}{a} e^{-\nu a^2 t} \right] \\ & + \frac{a^2}{\lambda_1} \frac{\partial}{\partial t} [\lambda_1 (\theta_x \sin az + \phi_x \cos az) e^{-\nu a^2 t}] \\ & + \nu a^4 \left[\left(\theta_x + \frac{\lambda_1}{a} \phi_y \right) \sin az \right. \\ & \left. + \left(\phi_x - \frac{\lambda_1}{a} \theta_y \right) \cos az \right] e^{-\nu a^2 t} = 0 \end{aligned} \quad (37)$$

Similarly by substituting the values of v_1 and v_2 from (35) and (36) in (27) we have

$$\begin{aligned} & \lambda_1 \frac{\partial}{\partial t} \left[\frac{a^2}{\lambda_1} (\theta_x \cos az - \phi_x \sin az) e^{-\nu a^2 t} \times \frac{\lambda_1}{a} \right] \\ & + \frac{a^2}{\lambda_1} \frac{\partial}{\partial t} [\lambda_1 (\theta_y \sin az + \phi_y \cos az) e^{-\nu a^2 t}] \\ & + \nu a^4 \left[\left(\phi_y + \frac{\lambda_1}{a} \theta_x \right) \cos az \right. \\ & \left. + \left(\theta_y - \frac{\lambda_1}{a} \phi_x \right) \sin az \right] e^{-\nu a^2 t} = 0. \end{aligned} \quad (38)$$

Equating the coefficients of $\cos az$ and $\sin az$ to zero separately in the above two equations we have, from (37)

$$\begin{aligned} a\lambda_1(-\theta_y)(-va^2) + a^2\phi_x(-va^2) + \frac{a^2}{\lambda_1}\phi_x\frac{\partial\lambda_1}{\partial t} \\ + va^4\left(\phi_x - \frac{\lambda_1}{a}\theta_y\right) = 0 \end{aligned}$$

and

$$\begin{aligned} a\lambda_1\phi_y(-va^2) + a^2\theta_x(-va^2) + \frac{a^2}{\lambda_1}\theta_x\frac{\partial\lambda_1}{\partial t} \\ + va^4\left(\theta_x + \frac{\lambda_1}{a}\phi_y\right) = 0 \end{aligned} \quad (39)$$

and from (38)

$$\begin{aligned} a\lambda_1\theta_x(-va^2) + a^2\phi_y(-va^2) + \frac{a^2}{\lambda_1}\phi_y\frac{\partial\lambda_1}{\partial t} \\ + va^4\left(\phi_y + \frac{\lambda_1}{a}\theta_x\right) = 0 \end{aligned}$$

and

$$\begin{aligned} a\lambda_1\phi_x(-va^2) + a^2\theta_y(-va^2) + \frac{a^2}{\lambda_1}\theta_y\frac{\partial\lambda_1}{\partial t} \\ + va^4\left(\theta_y - \frac{\lambda_1}{a}\phi_x\right) = 0. \end{aligned} \quad (40)$$

From (39) and (40) we get

$$\phi_x \frac{a^2}{\lambda_1} \frac{\partial\lambda_1}{\partial t} = 0; \quad \theta_x \frac{a^2}{\lambda_1} \frac{\partial\lambda_1}{\partial t} = 0, \quad (41)$$

$$\phi_y \frac{a^2}{\lambda_1} \frac{\partial\lambda_1}{\partial t} = 0; \quad \theta_y \frac{a^2}{\lambda_1} \frac{\partial\lambda_1}{\partial t} = 0. \quad (42)$$

Equations (41) and (42) give that for existence of the flows $\partial\lambda_1/\partial t$ must vanish, i.e., λ_1 must be an absolute constant.

Hence uniplanar superposable flows of the type $\text{curl } \mathbf{q}_1 = \lambda_2 \mathbf{q}_2$ and $\text{curl } \mathbf{q}_2 = \lambda_1 \mathbf{q}_1$ (where λ_1 and λ_2 are assumed to be independent of space variables) exist only if λ_1 and λ_2 are absolute constants.

The solution as obtained by Ballabh is, then,

$$\left. \begin{aligned} u_1 &= (\theta_x \sin az + \phi_x \cos az) e^{-\nu a^2 t} \\ v_1 &= (\theta_y \sin az + \phi_y \cos az) e^{-\nu a^2 t} \\ w_1 &= 0 \end{aligned} \right\}$$

$$\left. \begin{aligned} u_2 &= (\phi_y \sin az - \theta_y \cos az) \frac{\lambda_1}{a} e^{-\nu a^2 t} \\ v_2 &= (\theta_x \cos az - \phi_x \sin az) \frac{\lambda_1}{a} e^{-\nu a^2 t} \\ w_2 &= 0 \end{aligned} \right\}.$$

These belong to that class of uniplanar flows in which the ratio between the vorticity vector of one and velocity vector of the other is the same everywhere at all times. Their nature has already been discussed by Ballabh.

I am grateful to Dr. Ram Ballabh for supervising this work and to Scientific Research Committee, U.P., for financial assistance given to me.

REFERENCES

1. BALLABH, R. 1940, "Superposable Fluid Motions," *Proc. Benaras Math. Soc.*, **2**, (N.S.), 69-79.
2. —, 1943, "Fluid Motions of the type $\xi_1 = \lambda_2 u_2$, etc., and $\xi_2 = \lambda_1 u_1$, etc.," *Proc. Nat. Acad. Sci., India*, **13 A**, 151-58.

ADSORPTION OF GLUCOSE BY BENTONITE, SOIL AND OXIDES OF IRON AND ALUMINIUM

BY S. P. MITRA AND N. PANDA

(*Department of Chemistry, University of Allahabad, Allahabad*)

Received on January 3, 1957

SOIL polysaccharides have been shown to contain simple sugars, sugar acids,¹ sugar amines,² and methylated sugars.³ The sugars and its related compounds have been known to form complexes with montmorillonite⁴ and they are related to the soil polysaccharides which are thought to be highly important in the formation of good soil structure.^{5, 6} Bradley⁴ observed that the aqueous solutions of various organic compounds were adsorbed in the interlamellar region of the clay mineral, expelling water. Later work^{7, 8} has shown that this is only partially true. Complexes with basal spacings characteristic of the organic compounds are obtained when both water and organic compounds are present in the interlamellar regions. Greenland⁹ showed by X-ray diffraction studies of the adsorption of sugar by montmorillonite as well as the adsorption by chemical methods in which the concentrations of the sugar as well as the exchangeable cations have been found to affect the adsorption markedly. Ensminger and Pearson¹⁰ showed that the addition of montmorillonite clays to proteins and to a Florida peat was effective in rendering the material less susceptible to microbial decomposition under laboratory conditions. Moreover, montmorillonite exerted greatest effect in holding carbon whilst Kaolin exerted the least. In some cases the addition of 1% bentonite to the sand nearly doubled the quantity of residual carbon.

It is well known that bentonite is a montmorillonite mineral having the general formula $4\text{SiO}_2, \text{Al}_2\text{O}_3, \text{X H}_2\text{O}$. The alumina in the crystal lattice may partially be replaced by iron to give a material rich in iron. As soil contains both the clay minerals and the oxides of iron and aluminium, the present studies were made with a view to find out the adsorption of glucose by the soil. The adsorption of glucose by the oxides of iron and aluminium and bentonite have also been found out simultaneously. The photo-chemical oxidation of the various carbohydrates added to soil-studied, at Sheila Dhar Institute of Soil Science by Dhar and co-workers,¹¹ clearly shows that whole of the energy material added to the soil is not oxidised even after a period of 6-9 months. Hence it was thought worthwhile to find out the adsorption of soluble sugar like glucose by the soil.

EXPERIMENTAL

Five grams of powdered and oven-dried bentonite, soil, Fe_2O_3 and Al_2O_3 were taken in 250 c.c. flasks with 100 c.c. of glucose solution of different concentrations varying from 0.06 molar to 0.88 molar. Then the contents were shaken for 1 hour and allowed to stand for 24 hours at room temperature.

Next day the supernatant liquid was separated by filtering it through Buchner funnel fitted with a filter-paper. First few c.c. of the filtrate were rejected and then glucose contained in these solutions were estimated volumetrically by reduction of copper from an alkaline solution of copper-tartrate to cuprous oxide. The quantities of glucose contained in the original solutions were also determined. The difference in concentrations of the original and the equilibrium solutions were taken as the quantities of glucose adsorbed. The adsorption was calculated per 100 gm. of the material used.

RESULT

TABLE I

Adsorption of glucose by bentonite

	Original concentration (molar)	Equilibrium concentration (molar)	Quantities adsorbed by 5 gm.	Adsorption gm./100 gm.
1	0.8846	0.8654	0.3398	6.796
2	0.4422	0.4286	0.2457	4.914
3	0.2968	0.2869	0.1796	3.592
4	0.2156	0.2091	0.1169	2.338
5	0.1889	0.1839	0.0901	1.802
6	0.1643	0.1596	0.0850	1.700
7	0.1388	0.1361	0.0491	0.982
8	0.1197	0.1171	0.0467	0.934
9	0.1085	0.1060	0.0448	0.896
10	0.0977	0.0957	0.0364	0.728
11	0.0895	0.0873	0.0406	0.812
12	0.0793	0.0775	0.0319	0.638
13	0.0754	0.0738	0.0289	0.578
14	0.0687	0.0673	0.0241	0.482
15	0.0640	0.0625	0.0259	0.518

DISCUSSION

The foregoing results clearly show that the amount of glucose adsorbed from the aqueous solution increases as the concentration is increased from

TABLE II
Adsorption of glucose by soil

	Original concentration (molar)	Equilibrium concentration (molar)	Quantities adsorbed by 5 gm.	Adsorption gm./100 gm.
1	0.9018	0.8790	0.4110	8.22
2	0.4627	0.4538	0.1634	3.26
3	0.3197	0.3086	0.1006	2.01
4	0.2299	0.2269	0.0540	1.08
5	0.1876	0.1851	0.0450	0.90
6	0.1551	0.1534	0.0308	0.61
7	0.1331	0.1316	0.0270	0.54
8	0.1191	0.1176	0.0273	0.54
9	0.1062	0.1047	0.0255	0.51
10	0.0919	0.0907	0.0217	0.43
11	0.0814	0.0805	0.0170	0.34
12	0.0784	0.0775	0.0158	0.31
13	0.0726	0.0719	0.0136	0.27
14	0.0661	0.0655	0.0112	0.22
15	0.0625	0.0620	0.0101	0.20

TABLE III
Adsorption of glucose by aluminium oxide

	Original concentration (molar)	Equilibrium concentration (molar)	Quantities adsorbed by 5 gm.	Adsorption gm./100 gm.
1	0.9383	0.9225	0.2300	4.600
2	0.4822	0.4755	0.1189	2.378
3	0.3133	0.3083	0.0931	1.862
4	0.2400	0.2377	0.0444	0.888
5	0.1966	0.1938	0.0495	0.990
6	0.1650	0.1633	0.0350	0.700
7	0.1438	0.1422	0.0265	0.530
8	0.1216	0.1205	0.0190	0.380
9	0.1083	0.1072	0.0194	0.388
10	0.0988	0.0983	0.0127	0.254
11	0.0894	0.0888	0.0104	0.208
12	0.0794	0.0788	0.0163	0.326
13	0.0727	0.0722	0.0137	0.274
14	0.0677	0.0672	0.0119	0.238
15	0.0638	0.0633	0.0107	0.214

TABLE IV

Adsorption of glucose by ferric oxide

	Original concentration (molar)	Equilibrium concentration (molar)	Quantities adsorbed by 5 gm.	Adsorption gm./100 gm.
1	0.9644	0.9316	0.5826	11.65
2	0.4788	0.4538	0.4507	9.01
3	0.3100	0.2852	0.3936	7.87
4	0.2353	0.2295	0.1050	2.10
5	0.1863	0.1815	0.0872	1.74
6	0.1577	0.1542	0.0627	1.25
7	0.1322	0.1297	0.0445	0.89
8	0.1166	0.1138	0.0517	1.03
9	0.1043	0.1020	0.0421	0.84
10	0.0925	0.0907	0.0327	0.64
11	0.0853	0.0836	0.0277	0.55
12	0.0767	0.0754	0.0226	0.45
13	0.0709	0.0694	0.0255	0.51
14	0.0667	0.0655	0.0225	0.45
15	0.0598	0.0588	0.0182	0.36

0.06 molar to 0.9 molar, but the increase in adsorption is not directly proportional to an increase in the concentration of the solution used. The amount of glucose adsorbed by bentonite is greater than that obtained with the soil or Al_2O_3 , but is lesser than Fe_2O_3 at higher concentration (0.3 molar to 0.9 molar). However it is interesting to note that not more than 2% of the glucose added is in the adsorbed state. At lower concentration, on plotting the log values of equilibrium concentration and X/M a curve is obtained which clearly indicates the applicability of the Freundlich's Adsorption Isotherm.

Various mechanisms have been suggested for the adsorption of sugars by the clay minerals of which the most striking is the interlamellar adsorption as is clear from the X-ray diffraction studies. But from the chemical studies and the results as obtained by us, it is clear that the adsorption of glucose greatly depends on the amount Al_2O_3 and Fe_2O_3 . The soils and the clay minerals are equally well supplied with these two constituents and hence there is practically a similar adsorption of glucose by the soil, bentonite, Al_2O_3 and Fe_2O_3 . Thus Al_2O_3 and Fe_2O_3 seem to play an important role in the adsorption of glucose by forming complexes with it.

A similarity between the phosphate and glucose adsorption may also be suggested because the adsorption of phosphate follows the same trend with the difference that the percentage of phosphate adsorbed from the solution is higher in comparison to glucose. This may be due to a very small dissociation of glucose in aqueous solution. Also glucose may combine with the exchangeable bases present in the exchange complex of the soil and bentonite. Hendricks and Jefferson,¹² Mathieson and Walker¹³ have also suggested that hydrogen bonds may exist between the negatively charged sugar and clay just as between water and clay.

REFERENCES

1. FORSYTH, W. G. C., 1945, *Biochem. J.*, **41**, 176; *Ibid.*, 1950, **46**, 141.
2. BREMNER, J. M., 1950, *Ibid.*, **47**, 538.
3. DUFF, R. B., 1952, *J. Sci. Fd. Agric.*, **3**, 140.
4. BRADLEY, W. F., 1945, *J. Amer. Chem. Soc.*, **67**, 975.
5. MARTIN, J. P., 1946, *Soil Sci.*, **61**, 157.
6. GEOGHEGAN, M. J., 1950, *Trans. 4th Int. Cong. Soil Sci.*, **1**, 198.
7. GLAESER, R., 1948, *C.R. Acad. Sci. (Paris)*, **226**, 935.
8. MACKENZIE, R. C., 1948, *Trans. Farad. Soc.*, **44**, 368.
9. GREENLAND, D. J., 1956, *J. Soil Sci.*, **7**, 319-34.
10. ENSMINGER, L. E. AND PEARSON, R. W., 1950 *Advances in Agronomy*, **2**, 81-109.
11. DHAR, N. R., 1955, *Proc. Nat. Acad. Sci. (India)*, **24 A**, 531-34.
12. HENDRICKS, S. B. AND JEFFERSON, M. E., 1938, *Amer. Min.*, **23**, 813.
13. MATHIESON, A., MCL WALKER, G. F., 1954, *Ibid.*, **39**, 231.
14. EDWARD, G. MAHIN AND RALPH, H. CARR, *Quantitative Agricultural Analysis*, 157-58.

ADSORPTION OF GLUCOSE BY CALCIUM BENTONITE

By S. P. MITRA, S. G. MISRA AND N. PANDA

(Department of Chemistry, University of Allahabad, Allahabad)

Received on January 14, 1957

GREENLAND¹ has observed a marked effect of pH and exchangeable cations on the adsorption and fixation of glucose and sugar derivatives by the clay mineral montmorillonite. However we² independently began work on the adsorption of glucose by soils, bentonites and oxides of iron and aluminium in early July 1956. After observing high adsorptions of glucose by the above materials, experiments were started to find out the effect of saturating the bentonite with calcium. The present studies have been made with a view to investigate the adsorption of glucose by calcium bentonite.

EXPERIMENTAL

A bentonite sample from Kashmir was powdered very finely and then treated with normal calcium chloride solution. Next day the material was freed from chloride ions by washing repeatedly with distilled water and then oven-dried. It was again powdered, oven-dried and stored in corked bottles.

5 gm. of the above finely powdered calcium bentonite was taken in 250 c.c. conical flasks and 100 c.c. of glucose solutions of varying strength were added. The contents were shaken for one hour and then left for 24 hours.

Next day the filtration was completed in a Buchner funnel fitted with a filter-paper. The filtrates were analysed for their glucose concentrations. The original concentrations of the glucose solutions were also determined volumetrically by reduction of copper from an alkaline solution of copper-tartrate to cuprous oxide. The differences in the two concentrations gave the amount of glucose adsorbed by 5 gm. of the calcium bentonite. The adsorption was calculated per 100 gm. of the bentonite material.

Experiments on the adsorption of glucose by bentonite (without any treatment) were also carried side by side. The results have been given below. The amount of calcium coming into solution on treating the two bentonite materials with different concentrations of glucose solution have also been found in some cases by precipitating calcium as calcium oxalate and titrating it against standard KMnO_4 solution.

TABLE I

Adsorption of glucose by calcium bentonite

	Original concentration (molar)	Equilibrium concentration (molar)	Quantities adsorbed by 5 gm.		Adsorption gm./100 gm.	
			Ca Bentonite	Bentonite	Ca Bentonite	Bentonite
1	0.9383	0.9255	0.2250	0.3398	4.5	6.79
2	0.4691	0.4627	0.1120	0.2457	2.24	4.91
3	0.3100	0.3055	0.0740	0.1796	1.48	3.59
4	0.2294	0.2272	0.0410	0.1169	0.82	2.33
5	0.1861	0.1850	0.0220	0.0901	0.44	1.80
6	0.1538	0.1522	0.0300	0.0850	0.60	1.70
7	0.1294	0.1283	0.0220	0.0491	0.44	0.98
8	0.1138	0.1133	0.0180	0.0467	0.36	0.93
9	0.1016	0.1005	0.0200	0.0448	0.40	0.89
10	0.0910	0.0906	0.0070	0.0364	0.14	0.72
11	0.0816	0.0811	0.0080	0.0406	0.16	0.81
12	0.0754	0.0750	0.0070	0.0319	0.14	0.63
13	0.0710	0.0706	0.0060	0.0289	0.12	0.57
14	0.0683	0.0680	0.0050	0.0241	0.10	0.48

TABLE II

Calcium given out in the extracts of calcium bentonite and bentonite

Glucose concentration (molar)	Glucose solution used (in c.c.)	CaO given out in m.e./100 gm. from	
		Ca Bentonite	Bentonite
0.500	100	11.3	Trace
0.250	100	11.3	"
0.166	100	9.4	"
0.125	100	10.4	"
0.100	100	8.4	"
Distilled water	100	7.1	"

DISCUSSION

From the foregoing results it is clear that the adsorption of glucose by bentonite is decreased very markedly on converting it into a calcium bentonite. It is practically $\frac{1}{2}$ – $\frac{1}{4}$ at lower concentrations. The adsorption of glucose goes on increasing as its concentration is increased but the increase is in no way directly proportional to an increase in the concentration of glucose solution. On plotting the logarithms of the original and equilibrium concentrations of glucose, in the case of calcium bentonite a very regular curve is obtained whilst the curve is not so regular with bentonite alone. It appears, therefore, that calcium bentonite obeys the Freundlich's adsorption isotherm very strictly.

But one very peculiar contrast is observed when we compare the amounts of calcium coming into solution on treating the two bentonite materials with glucose solutions. Greater quantities of calcium are present in the glucose extracts of the calcium bentonite and the quantities have the tendency to decrease with a decrease in the glucose concentration used for adsorption. However no regular behaviour is observed. As the amounts of calcium in glucose solution are always greater than those present in the water extract of the calcium bentonite, it appears that glucose forms a complex with calcium which is more soluble than the calcium of the untreated bentonite. By treating the bentonite with calcium chloride, the adsorption of glucose is invariably decreased.

Further experiments are in progress using barium and strontium bentonites.

REFERENCES

1. GREENLAND, D. J., 1956, *J. Soil Sci.*, **1**, 329–34.
2. MITRA, S. P. AND PANDA, N., 1957, *Proc. Nat. Acad. Sci., (India)*, **26 A**.

IDENTIFICATION OF CLAY MINERALS OF INDIAN ORIGIN

BY S. P. MITRA AND DHARAM PRAKASH

(*Department of Chemistry, University of Allahabad, Allahabad*)

Received on June 4, 1956

IDENTIFICATION and estimation of minerals is one of the most difficult problems in mineral chemistry. Chemical analysis alone does not convey any definite idea of the nature of the mineral due to various reasons, chief amongst them being the difficulty of obtaining absolutely pure minerals. If, however, the nature of the principal minerals have already been determined by other physical methods, *e.g.*, X-ray diffraction and differential thermal analysis, the bulk chemical composition may be interpreted in terms of relative quantities of the component minerals, but how accurately this can be done depends largely on the kind and number of minerals involved and especially on the variability of their composition due to isomorphous replacement.

Chemical analysis of minerals vary widely as reported by different workers (Tables I-III). Chemical analysis of minerals of Indian origin along with the analysis of the same minerals obtained from Ward's Natural Science Establishment Inc. of U.S.A. are given in Table IV. This only shows approximate similarity of the Indian and foreign minerals. Moreover, a comparison of analysis of Georgia Kaolinite and Wyoming Bentonite done by the authors and other workers shows wide variation in chemical composition. This conclusively proves that chemical analysis of minerals cannot be used for identifying them. Different methods for identifying the minerals include X-ray diffraction, electron microscopy, differential thermal analysis, dehydration curves, refractive index determinations, determinations of specific gravity, fractionation according to particle size, determination of cation exchange capacity and characteristic of titration curves. In general several methods must be used to attain any degree of certainty as to purity.

The present investigation was undertaken with a view to make the identification of clay minerals by chemical, differential thermal and X-ray methods. An attempt has been made in this paper to prove the identity of the three minerals kaolinite, bentonite and vermiculite of Indian origin by comparing their differential thermal analysis curves and X-ray diffraction patterns with those of the same minerals obtained from foreign sources.

EXPERIMENTAL

The chemical analysis of the minerals was done by the fusion method as described by Washington.¹

The differential thermal analysis of minerals was studied in an apparatus manufactured by Eberbach Corporation of U.S.A. Inert material (calcined alumina) and the minerals were ground in an agate pestle and mortar to pass through 100-mesh sieve. A nickel block with cavities for inert material and unknown mineral was used. Chromal-alumel thermocouple wire was used and the heating rate was maintained at 10° C./min. The samples were packed very hard and then a few holes were made for the escape of gases. During the experiment, the samples were covered by nickel plates.

For X-ray diffraction studies, Philips X-ray diffraction apparatus (PW 1009) has been used. The samples of minerals were mounted in Lindemann glass capillaries of 0.5 mm. diameter in 18 cm. diameter camera. Mono-chromatic radiation $\text{CuK}\alpha$ (with nickel filter) was used at 20 mA and 35 KV and the samples were exposed for 4 hours. The water pressure was maintained at 40 lb.

RESULTS

TABLE I

Chemical analysis of vermiculite

	1	2	3	4
	Maryland (Bare Hills)	Maryland (Pilot)	North Carolina	Kenya
SiO_2	.. 36.12	35.92	36.54	34.04
Al_2O_3	.. 13.90	10.68	16.96	15.37
Fe_2O_3	.. 4.24	10.94	2.78	8.01
FeO	.. 0.68	0.82	0.95	..
MgO	.. 24.84	22.00	19.78	22.58
CaO	.. 0.18	0.44	0.06	..
TiO_2	.. 0.24
H_2O	.. 18.94	19.84	20.40	19.93

Analysis 1-3 from J. W. Gruner, *Am. Mineral*, **19**, 557-75 (1934).

Analysis 4 from G. F. Walker and A. Milne, *Trans, 4th Int. Cong. Soil Sci.*, 1950, **2**, 62.

TABLE II
Chemical analysis of montomorillonite

	1 Washing- ton (Manito)	2 North Carolina (Sandy Ridge)	3 Washing- ton (Spokane)	4 France (Nontron)	5 Wyoming	6 England (Nutfield)
SiO ₂	40.54	41.38	46.06	44.0	57.49	52.98
Al ₂ O ₃	5.19	9.84	12.22	3.6	20.27	12.87
Fe ₂ O ₃	31.24	27.47	18.54	29.0	2.92	3.97
FeO	0.39	Trace	0.28	..	0.19	2.78
MgO	0.06	..	1.62	2.1	3.18	2.67
CaO	1.92	..	1.66	..	0.23	2.54
K ₂ O	0.24	0.28	0.58
Na ₂ O	0.14	1.38	0.23
TiO ₂	0.84	..	0.12	0.53
H ₂ O	20.75	21.35	17.26	18.7	14.48	14.74

Analysis from P. F. Kerr, *Rep. No. 7, A.P.I. Project 49, 1950.*

TABLE III
Chemical analysis of kaolinite

	1 Czecho- slovakia (Zettlitz)	2 Mexia (Texas)	3 Georgia (Macon)	4 England (St. Austell)	5 Illinois (Auna)	6 Germany Holzhsh- ausen	7 France Echassieres
SiO ₂	46.90	44.81	45.20	46.77	44.59	45.93	48.00
Al ₂ O ₃	37.40	37.82	37.02	37.79	36.83	33.31	35.65
Fe ₂ O ₃	0.65	0.92	0.27	0.45	1.14	0.87	0.74
FeO	0.06	0.11	..	0.23	0.31
MgO	0.27	0.35	0.47	0.24	0.39	0.44	0.22
CaO	0.29	0.43	0.52	0.13	1.02	0.51	0.13
K ₂ O	0.84	..	0.49	1.49	0.32	1.30	2.15
Na ₂ O	0.44	..	0.36	0.05	0.13	0.20	0.22
TiO ₂	0.18	0.37	1.26	..	2.17	3.17	0.05
H ₂ O	12.95	15.37	14.82	12.79	13.63	13.16	11.53

Analyses 1 and 2 from C. S. Ross and P. F. Kerr, *U.S. Geo. Survey Professional Paper 165 E*, 1931,

Analyses 3, 4, 6 and 7 from P. F. Kerr, *Report No. 7, A.P.I. Project No. 49, 1950,*

Analysis 5 from R. E. Grim, *Econ. Geol.*, 1934, 29, 659-70.

TABLE IV

Chemical analysis of minerals by the authors

		Vermiculite (Mysore)	Vermiculite (Montana)	Bentonite (Kashmir)	Bentonite (Wyo- ming)	Kaolinite (Jubbulpore)	Kaolinite (Georgia)
SiO ₂	..	39.840	46.00	54.560	58.450	53.900	51.276
Al ₂ O ₃	..	9.280	17.30	20.500	27.650	37.600	36.179
Fe ₂ O ₃	..	20.400	9.00	2.200	4.200	1.400	2.379
P ₂ O ₅	..	0.169	Trace	0.013	0.032	0.140	0.266
K ₂ O	..	4.450	5.08	0.624	1.529	0.106	0.153
MgO	..	11.850	14.42	5.680	2.020	0.833	0.739
CaO	..	1.770	3.15	2.240	1.400	0.490	0.466

The results of differential thermal analysis of minerals are recorded in Fig. 1. Peak temperatures observed for the different minerals are as follows:—

TABLE V

Mineral	Peak temperatures
Wyoming Bentonite ..	160° C. and 725° C.
Kashmir Bentonite ..	190° C. and 770° C.
Georgia Kaolinite ..	680° C. and 970° C.
Jubbulpore Kaolinite ..	740° C. and 950° C.
Mysore Vermiculite ..	220° C. and 360° C.
Montana Vermiculite ..	190° C. and 320° C.

DISCUSSION

The results recorded in Tables I-IV show the chemical composition of the various minerals occurring in different parts of the world. There is a

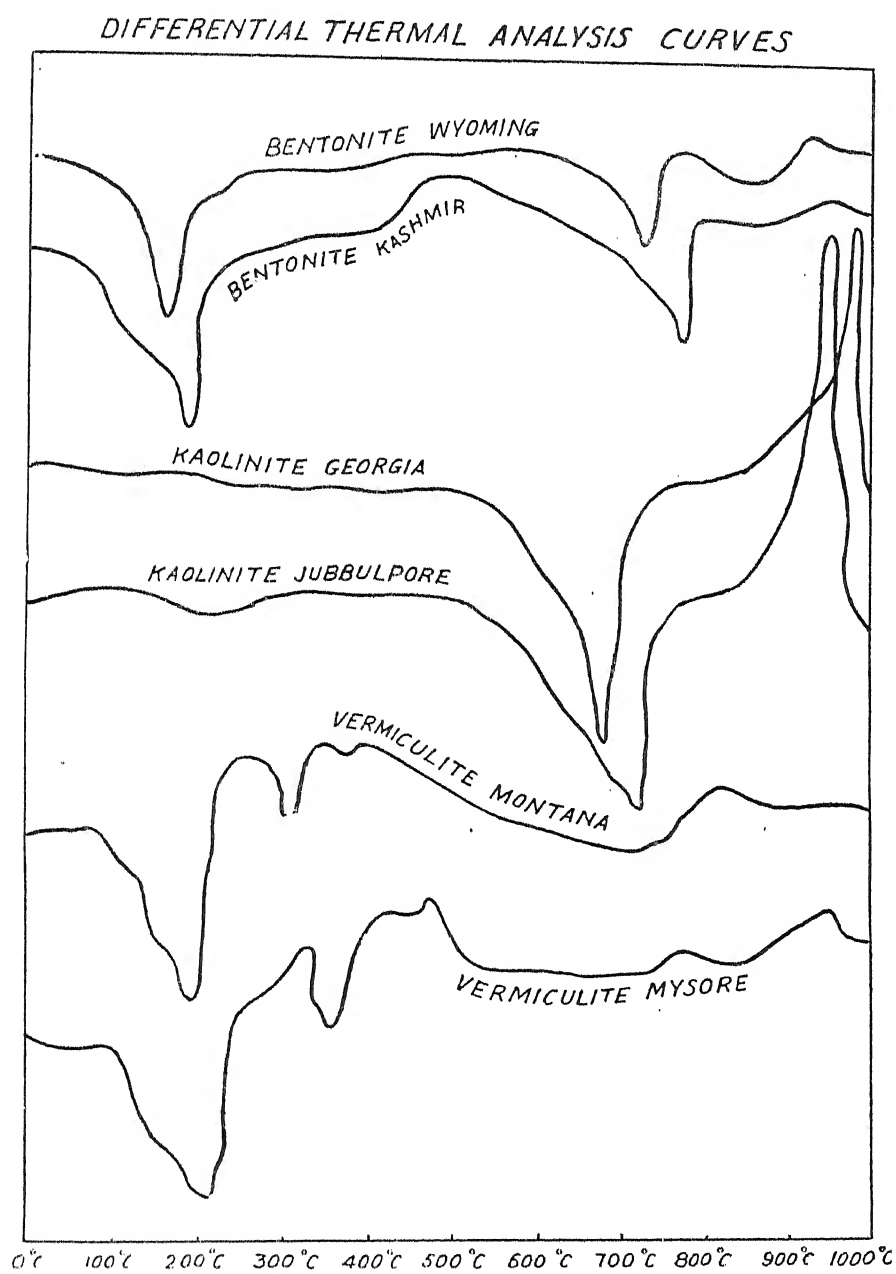


FIG. 1

wide variation in the chemical constituents of these minerals and it is not possible to draw any conclusion regarding the identity of these clay minerals. The differential thermal analysis curves of the same mineral obtained by any

two workers do not agree due to the variation in the experimental technique. As the method has proved so valuable, a serious attempt is at present being made by the D.T.A. Sub-Committee of the Comité International pour l'Étude des Argiles to correlate results for different types of apparatus by distributing a series of "standard" minerals and comparing the results obtained. These minerals are only "standard" in the sense that the samples sent to each laboratory were identical and no claim is made for mineralogical purity, although this was generally high. The results show surprising difference, e.g., for kaolinite, peak temperature obtained by various workers vary from 573° C. to 650° C. and for Wyoming bentonite from 689° C. to 750° C.

The shape of the D.T.A. curve of Indian and the corresponding foreign minerals run on the same apparatus is practically the same. The peak temperatures for these minerals obtained are also within the range reported by other workers. The small difference in peak temperatures between Indian and foreign minerals may be ascribed to impurities and it can be concluded that the Indian minerals used are substantially pure.

Figure 2 (a) shows the X-ray diffraction pattern of Montana vermiculite, while Fig. 2 (b) shows the X-ray diffraction pattern of Mysore vermiculite. It will be seen that the main lines of both the photographs are the same, proving their identity. The extra lines in the case of Mysore vermiculite may be due to impurities. Exactly similar X-ray diffraction photographs were obtained in the case of bentonite from Kashmir and Wyoming and kaolinite from Jubbulpore and Georgia showing thereby that the Indian minerals are the same as that obtained from foreign sources.

REFERENCES

1. WASHINGTON, H. S., 1930, *The Chemical Analysis of Rocks*, 4th Edition.
2. MACKENZIE, R. C., 1949, *Nature*, **164**, 244.
3. WALKER, G. F. AND HART, R., 1949, *Min. Mag.*, **28**, 704.
4. GRIM, R. E. AND ROWLAND, R. A., 1942, *Amer. Min.*, **27**, 746.

*S. P. Mitra and
Dharam Prakash*

Proc. Nat. Acad. Sci., A, Vol. 26, Part 1

INFLUENCE OF MAGNESIUM IONS ON THE PHYSIOLOGICAL PROPERTIES OF DHAR YEAST

BY KRISHNA BAHADUR

(Department of Chemistry, University of Allahabad, Allahabad)

Received on November 7, 1956

MAYER¹ from his experiments found that magnesium is an essential element in the culture for the best growth of yeast. His investigations showed that magnesium is the next important mineral nutrient of yeast after potassium and phosphate. Elion² and Stern³ confirmed Mayer's results and proved that magnesium is indispensable for the life of yeast. On the other hand Booy⁴ holds that magnesium has no effect on the fermentation of yeast up to about 1 N.

This discrepancy between these findings might possibly be due to the fact that the presence of magnesium does not affect the growth of yeast whereas its metabolism is greatly influenced by the element. The formation of microbial enzymes is as a rule profoundly influenced by the availability of metallic ions.⁵ And this effect on enzyme formation is shown by alterations in physiological activities of the organisms.

There have been a few contributions of late towards an understanding of the role of magnesium in the metabolism of plants.⁶ It is becoming increasingly evident that magnesium deficiency may be a prime consideration in crop production. Chlorosis and other abnormal pigmentation patterns of leaves associated with magnesium deficiency have been recently reported on pears,⁷ apples⁸ and tomatoes.^{9, 10}

While studying the role of magnesium ions in the culture of *Clostridium perfringens* Shankar and Bard¹¹ have reported that due to the absence of magnesium ion in the culture, cell division appears to be inhibited, since filamentous cells are produced. Webb¹² has found that the growth of bacteria is less dependent on magnesium in chemically defined media containing mixtures of amino acids as compared to media with a single source of nitrogen.

But there are other phases of nutrition which are important and which in many instances have so far not received the systematic investigation which they merit. Thus there are the subtler aspects of nutrition in which a nutrient may have little or no effect on the extent of growth but may greatly stimulate

the rate of growth, more importantly exert a profound influence on metabolic processes such as the formation of specific enzymes pigments, toxins and others.¹³ In this paper, the influence of magnesium ions on the metabolism of Dhar yeast¹⁴ has been studied from this view-point. Observing the influence of magnesium ions in the culture on the growth of yeast only, it appears that the concentration of magnesium does not affect the growth of yeast much, but it profoundly influences the metabolic activity of this organism.

I have studied these changes in the physiological properties of Dhar yeast in the presence of different concentrations of magnesium ions in the cultures, by analysing the various metabolic products that have been recovered from the mixture at the end of the experiment.

EXPERIMENTAL

To five 750 ml. flat bottom flasks, each of which contained 0.2 gm. calcium carbonate, 0.2 gm. of sodium chloride, 0.2 gm. of potassium sulphate, 0.2 gm. of disodium hydrogen phosphate and 2.5 gm. of ammonium sulphate, were added the amounts of magnesium carbonate mentioned in the tables below. These substances were dissolved in the minimum amount of dilute hydrochloric acid and 20 gm. of sucrose were added to each. The total volume of each culture medium was made up to 400 c.c. with the addition of distilled water meanwhile adjusting the pH to 4.5. The flasks were cotton-plugged and sterilised by heating at 10 lb. pressure for 30 minutes in an autoclave. After cooling the culture media were seeded with a trace of an activated sample of Dhar yeast which was prepared by growing the yeast in normal yeast culture for two days. This sample of yeast used for seeding was tested for its purity by growing it in yeast cultures. No bacterial growth was observed in such cultures even after several days, when the yeast was examined under the microscope.

All the cultures were kept together at room temperature under non-aerated conditions. They were analysed after 30 days. During this period the yeast cells remained healthy and did not show any sign of putrefaction or autolysis. The temperature variation during this period was between 22.2° C. to 23.9° C.

Estimation of nitrogen in these cultures was carried out by Kjeldahl and Gunning's method.¹⁵⁻¹⁹ To estimate the amount of nitrogen left in the culture solution, 100 c.c. of the clear solution obtained by filtering off the yeast cells were dried to almost dryness in a Kjeldahl flask. To this residue were added 5 gm. of potassium sulphate, 1 gm. of salicylic acid,

0.2 gm. of copper sulphate and 20 c.c. of concentrated sulphuric acid and the mixture was boiled till it became clear. This clear solution was distilled in the presence of excess of alkali and the ammonia thus set free was estimated. The distillation apparatus was made absolutely air-tight as was confirmed by the correct results which were obtained by the analysis of a few known pure compounds.

To estimate the nitrogen in yeast cells a known weight of yeast dried at 60° C. was digested with concentrated sulphuric acid in the presence of copper sulphate and potassium sulphate and then the amount of nitrogen was estimated as mentioned above. All the chemicals used for analysis and in the preparation of culture solutions were of A.R. quality. As the results obtained in these experiments are extremely interesting, the experiments were repeated three times with the same results.

OBSERVATIONS

Sugar consumed

S. No.	Magnesium carbonate added to 400 c.c. of culture medium (gm.)	Percentage concentration of Mg	Reducing sugar left in the culture medium (gm.)	Total sugar left in the culture medium (gm.)	Total sugar consumed	Percentage of sugar consumed
1	0.1000	0.0071	5.28	5.48	14.52	72.6
2	0.2500	0.0178	5.32	5.52	14.48	72.4
3	0.5000	0.0356	5.56	5.56	14.44	72.2
4	0.7500	0.0534	7.64	7.64	12.36	61.8
5	1.0000	0.0712	7.12	7.48	12.52	62.6

The loss of alcohol from the cultures due to evaporation through the cotton plugs was determined as follows. 400 c.c. of very dilute standard solutions of ethyl alcohol in water were taken in similar flasks and cotton plugged and kept under the same conditions as the cultures. These solutions were analysed for their alcohol contents along with the culture solutions and a graph was drawn indicating the relationship between concentration and evaporation of alcohol. With the help of this, the loss of alcohol in each culture was evaluated. The amounts of alcohol given indicate the alcohol formed after evaporation correction.

Yeast obtained and acid and alcohol formed

S. No.	Percentage concentration of Mg	Total acid(s) formed (gm. eqvt.)	Percentage of acid formed	Yeast produced (gm. dry weight)	Efficiency of yeast formation (% of yeast formed per gm. sugar consumed)	Ethyl alcohol formed (gm.)	Percentage of alcohol formed per gm. of sugar consumed
1	0.0071	1.5308	10.54	3.8240	26.39	0.60	4.13
2	0.0178	1.5474	10.63	3.9964	27.70	0.60	4.14
3	0.0356	1.5142	10.65	3.8180	26.44	0.60	4.15
4	0.0534	1.5808	12.96	3.6248	29.32	0.60	4.85
5	0.0712	1.6804	13.42	2.8916	23.14	0.00	0.00

Nitrogen balance sheet

S. No.	Percentage of Mg	A Nitrogen left in the culture (gm.)	B Nitrogen consumed (gm.)	C Nitrogen recovered in yeast cells produced	(C - B) gm. of nitrogen fixed or lost represented by - or +	Do. per gm. of yeast	Nitrogen content of yeast cells produced (% of dry wt.)
1	0.0071	0.1676	0.3514	0.2092	-0.1430	0.0373	5.46
2	0.0178	0.1698	0.3610	0.2082	-0.1522	0.0380	5.21
3	0.0356	0.3528	0.1776	0.2192	+0.0216	+0.0066	5.95
4	0.0534	0.3666	0.1638	0.2482	+0.0844	+0.0234	6.85
5	0.0712	0.4104	0.1204	0.2362	+0.01156	+0.0400	8.16

Initial concentration of nitrogen in the culture medium 0.5303 gm.

INFERENCES

The growth of the yeast was not much affected on increasing the amount of Mg^{++} in the culture medium. At a very high concentration of 0.712% Mg^{++} , however, a slight decrease in the yield was observed.

A small increase in the concentration of Mg^{++} in the culture medium did not affect the sugar consumption. Above 0.0356% Mg^{++} a slight decrease in the sugar consumption was noticed.

The acid production is also not much influenced upto 0.0356% Mg^{++} in the culture medium, at higher Mg^{++} concentration, slight increases in acid formation were observed. Yield in alcohol remained constant upto 0.0534% Mg^{++} in the culture medium; at higher concentration of Mg^{++} (0.0712%) no alcoholic fermentation whatever was observed.

The nitrogen metabolism of the yeast was most profoundly influenced by the concentration of Mg^{++} in the medium. When the concentration of Mg^{++} in the culture is less, a loss of nitrogen is seen in the cultures. Unnegligible discrepancies between the amount of nitrogen consumed from the culture medium and that recovered in yeast cells harvested were observed. The differences were always in favour of the yield of nitrogen with higher Mg -concentrations; at lower concentrations of Mg^{++} . Considerable loss in the nitrogen balance sheet was indicated. As to the cause of the above said discrepancies, no final conclusion was yet obtained.

The nitrogen content of the yeast and consequently the protein content markedly increase with the increase in the concentration of Mg^{++} in the culture medium. Thus calculated, the yeast which has grown in a medium containing 0.0071% Mg^{++} showed a nitrogen content of 5.46% whereas in a medium containing 0.0712% Mg^{++} it amounted to 8.16%N.

SUMMARY

Variations in the amounts of Mg^{++} added to the culture of Dhar yeast did not markedly affect the growth of yeast, the consumption of sugar and the formation of alcohol and acids. On the other hand, the concentration of Mg^{++} in the medium had a profound influence on the nitrogen metabolism of the yeast. With lower concentrations of Mg^{++} in the culture medium, loss of nitrogen was indicated. While at higher Mg^{++} concentrations more and more favourable figures in the fixation of nitrogen was observed. The nitrogen content of the yeast cells was conspicuously increased at higher concentrations of Mg^{++} to attain finally a value of 8.16%N at a Mg^{++} concentration of 0.0712%.

ACKNOWLEDGMENT

My sincere thanks are due to Prof. N. R. Dhar for his valuable advice in carrying out these experiments.

REFERENCES

1. MAYER, A., *Lehrbuch der Gärungschemie*, 1902 edition.
2. ELION, H., 1893, *Studien über Hefe*, *Cent. Bakt.*, **14**.
3. STERN, 1899 and 1901, "Nutrition de la levre," *Jour. Chem. Society*.
4. BOOY, H. L., 1940, *Rec. trav. botan. Neerland*, **1**, 37.
5. STOKES, J. L., 1952, *Ann. Rev. Microbiol.*, **6**, 39.
6. WADLEIGH, C. H., 1949, *Proc. Ann. Rev. Biochem.*, **18**, 663.
7. HARLEY, C. P., 1947, *Proc. Am. Soc. Hort. Sci.*, **50**, 21-22.
8. CAIN, J. C. AND BOYNTON, D., 1948, *Ibid.*, **51**, 1-12.
9. HESTER, J. B., SMITH, G. C. AND SHELTON, F. A., 1947, *Ibid.*, **49**, 304-08.
10. NICHOLAS, D. J. D., 1948, *J. Hort. Sci.*, **24**, 1-18.
11. SHANKAR, K. AND BARD, R. C., 1952, *J. Bact.*, **63**, 279-90.
12. WEBB, M. J., 1951, *Gen. Microbiol.*, **5**, 486-95.
13. STOKES, J. L., 1952, *Ann. Rev. Microbiol.*, **6**, 44.
14. DHAR, N. R. AND KRISHNA BAHADUR, 1950, *Proc. Nat. Acad. Sci., India*, **19 A** (2), 55-60.
15. KJELDAHL, J., 1883, *Z. Anal. Chem.*, **22**, 366.
16. GUNNING, J. W., 1889, *Anal. Chem.*, **28**, 188.
17. ARNOLD, C., 1886, *Chem. Zentr.*, 377.
— AND WEDENMEYER, K., 1892, *Z. Anal. Chem.*, **31**, 525.
18. KOLTHOFF, I. M. AND STENGER, B. A., 1947, *Procedure of Volumetric Analysis*, p. 173.
19. MOORE, H. C., 1920, *Ind. Eng. Chem.*, **12**, 669.
PRINCE, A. L., 1925, *J. Assoc. Official Agr. Chem.*, 410.

EDITORIAL BOARD

1. ~~PROF. P. S. GILL~~, Allgarh (*Chairman*).
2. „ K. BANERJI, Allahabad.
3. „ RAM BEHARI, Delhi.
4. „ P. L. SRIVASTAVA, Allahabad.
5. „ S. GHOSH, Allahabad.
6. „ A. K. BHATTACHARYA, Saugor.
7. „ N. R. DHAR, Allahabad.
8. „ S. RANJAN, Allahabad.
9. „ R. MISRA, Banaras.
10. „ M. D. L. SRIVASTAVA, Allahabad.
11. „ W. D. WEST, Saugor.
12. DR. S. P. RAYCHAUDHURI, New Delhi.
13. „ R. K. SAKSENA, Allahabad.
14. „ R. N. TANDON, Allahabad (*Secretary*).

CONTENTS

	PAGE
On the Maximum Attainable Stellar Luminosities Harlow Shapley	1
Reclamation of Alkali Soils by Mixtures of Phosphates and Sunn-Hemp S. P. Mitra and Raghubir Singh	6
On Choice of Internal Standard in Quantitative Spectro-Chemical Analysis J. K. Zope and J. D. Ranade	15
Composition and Stability of Lead Alizarin Sulphonate Complex: A Spectro- photometric Study Anil K. Mukherji and Arun K. Dey	20
An Inversion Formula for the Third Iterate of Laplace Transform. B. B. Misra	37
Physico-Chemical Studies in the Formation of Trivalent Manganese. Part I. Oxidation of Manganese II Sulphate by Potassium Dichromate Dharendra Nath Chakravarty and Satyeshwar Ghosh	41
Effect of Acids on the Rate of Reaction between Formic Acid and Chromic Acid—Part II. A. V. Mahajani	49
Comparative Study of the Activation of Papain by Bisulphite and Ammonium Ions Ramesh Chandra Sinha and Krishna Bahadur	53
Superposable Flows of the Type $\text{Curl } q_1 = \lambda_2 q_2$ and $\text{Curl } q_2 = \lambda_1 q_1$ C. D. Ghildyal	58
Adsorption of Glucose by Bentonite, Soil and Oxides of Iron and Aluminium S. P. Mitra and N. Panda	67
Adsorption of Glucose by Calcium Bentonite S. P. Mitra, S. G. Misra and N. Panda	72
Identification of Clay Minerals of Indian Origin S. P. Mitra and Dharam Prakash	75
Influence of Magnesium Ions on the Physiological Properties of Dhar Yeast Krishna Bahadur	81